

**ELECTRONIC THEORY
FOR THE ATOMIC STRUCTURE AT THE
SURFACE OF TRANSITION METALS AND ALLOYS:
SEGREGATION AND CHEMISORPTION EFFECTS**

**(Elektronische Theorie für die atomare Struktur an Oberflächen
von Übergangsmetallen und Legierungen:
Segregations- und Chemisorptionseffekte)**

Thesis submitted for the Degree
DOCTOR RERUM NATURALIUM
at the Fachbereich Physik of the
Freie Universität Berlin

by
Sugata Mukherjee
from Calcutta, India

1985



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549615_0013

Druck: Copy-Center in Dahlem
Ladenbergstraße 2-4
1000 Berlin 33
Tel. 831 40 25

ELECTRONIC THEORY FOR THE ATOMIC STRUCTURE AT THE
SURFACE OF TRANSITION METALS AND ALLOYS :
SEGREGATION AND CHEMISORPTION EFFECTS

(Elektronische Theorie für die atomare Struktur an Oberflächen
von Übergangsmetallen und Legierungen :
Segregations- und Chemisorptionseffekte)

Thesis submitted for the Degree
DOCTOR RERUM NATURALIUM
at the Fachbereich Physik of the
Freie Universität Berlin

by

Sugata Mukherjee
from Calcutta, India

1985

1. Referent: Prof. Dr. K. H. Bennemann

Institut für Theorie der Kondensierten Materie (WE5)

Fachbereich Physik der Freien Universität Berlin

Arnimallee 14, 1000 Berlin 33.

2. Referent: Prof. Dr. J. Koutecký

Institut für Physikalische Chemie

Fachbereich Chemie der Freien Universität Berlin

Takustr. 3, 1000 Berlin 33.

Tag der Promotion : 29. Oktober 1985.

ACKNOWLEDGEMENTS

I am very much obliged to Prof. Dr. K. H. Bennemann, under whose supervision this work has been carried out, for his continued guidance, suggestions, support, encouragement and for his willingness for frequent discussions throughout the course of this work.

I am thankful to Prof. Dr. J. Koutecký for his interest in this work and useful discussions. I have also benefited from many useful discussions with my friends and colleagues, including, Dr. V. Kumar, Dr. J. L. Morán-López, Dr. D. Tománek, Dr. S. K. Ghatak, Mr. H. J. Brocksch and Mr. R. Linke. I thank them and also all other members of the Institute for their help and cooperation.

The computer time for the calculations was generously provided by the Computer Center (ZEDAT) of the Free University at their CDC Cyber-170/835 machine and by the Wissenschaftliches Rechenbetrieb (WRB) at Cyber-175 and CRAY-1M machines. Financial assistance from the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 6 is gratefully acknowledged.

Table of contents

1. INTRODUCTION	1
2. ELECTRONIC THEORY FOR THE SURFACE SEGREGATION AND SURFACE CORE-LEVEL-SHIFT IN TRANSITION METAL ALLOYS	12
2.1. Theory of surface segregation in transition metal alloys	12
2.1.1. Model	14
2.1.2. Calculation of surface segregation in Cu-Ni alloy	18
2.2. Theory of surface core-level-shift in alloys and its relationship to segregation	24
2.2.1. Calculation of surface core-level-shift for Cu-Ni alloy	28
2.3. Discussion of the results	30
3. THEORY FOR THE CHEMISORPTION, ABSORPTION AND SAMPLE SIZE INDUCED CHANGES IN SURFACE SEGREGATION IN BINARY METAL ALLOYS	33
3.1. Chemisorption induced segregation in alloys	34
3.2. Segregation in small clusters of alloys	39
3.3. Absorption induced surface segregation in alloy : H / Pd_xZr_{1-x}	46
3.4. Discussion of the results	51
3.4.1. A general ternary interface problem	55

4. ELECTRONIC THEORY OF CHEMISORPTION AND ITS APPLICATION IN INTERPRETING COMPOUND FORMATION TENDENCIES AT TRANSITION METAL SURFACE : OXYGEN AND SULFUR ON Ni(100)	58
4.1. Introduction	58
4.2. Theory of chemisorption on transition metals	62
4.2.1. Hamiltonian of the substrate-adsorbate system	64
4.2.2. Expression for the chemisorption binding energy	66
4.3. Method of calculation and choice of parameters	69
4.4. Results and discussions	72
4.4.1. Clean Ni (100) surface	72
4.4.2. Oxygen on Ni(100)	75
4.4.2.1. Repulsive interaction between adsorbed oxygen at high coverage	81
4.4.2.2. Formation of overlayers and NiO	83
4.4.3. Results for sulfur on Ni(100)	85
5. CONCLUSIONS AND OUTLOOK	89
APPENDIX A : Expression for the diagonal Green's function at alloy surface in Bethe-lattice approximation	94
APPENDIX B : Elements of the recursion method for calculating the local density-of-states	100
APPENDIX C : Expression for the change in Coulomb and exchange-correlation energies due to chemisorption	107
REFERENCES	111

1. INTRODUCTION

In recent years there has been a tremendous growth in the field of surface science, due to increasing development of various surface spectroscopic techniques. A surface can be defined as the boundary between any two states of the matter. In this work we shall confine ourselves to the surfaces of transition-metals and their alloys. The atoms at the crystal surface are not bonded to as many neighbors as in bulk, they can also have a different geometric arrangement compared to the bulk (Fig. 1.1). Like in the bulk, there may also be foreign atoms (impurities) and defects on the surface. These can change both microscopic and macroscopic properties like - catalysis, crystal growth, oxidation, segregation (in case of alloys) etc.

The electronic structure at the surfaces of transition-metal has been extensively studied in recent past /1,2/, but a complete understanding of all the mechanism occurring at the surface are not available. Particularly, in the case of alloy surfaces theoretical studies on the behavior of valence electrons is still limited.

It is well known that the surface composition of metal alloys may differ from that in bulk. This property, known as surface

Vacuum

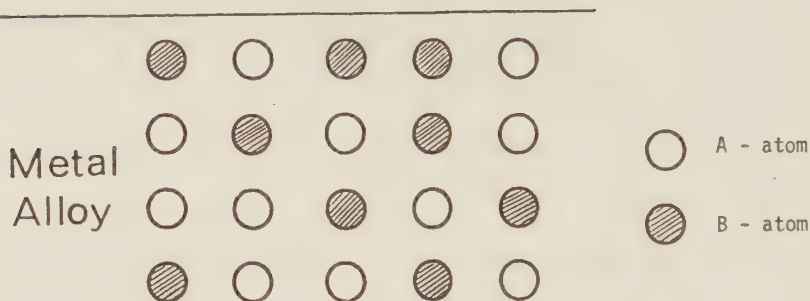


Fig.1.1: Illustration of the alloy and vacuum interface model used in this discussion.

segregation, plays a very important role in the catalytic property of the alloys /3-5/. Generally, the role of a catalyst in a chemical reaction is to break a certain kind of chemical bonds between the catalyst and reactant atoms. In case of bimetallic catalysts this situation is achieved by changing the concentration of atoms in the catalyst, so that the catalytic activity of the alloy varies with its composition. There exists extensive measurements of the concentration dependence of the acitivity of bimetallic catalysts like Cu-Ni, Ru-Cu, Os-Cu etc. /5-7/.

In order to explain the catalytic behavior of the alloy catalyst it is very important to investigate the actual surface composition of the alloy as a function of its bulk composition. Using experimental techniques like selective chemisorption /8/, Auger electron spectroscopy (AES) /9,10/, low-energy ion scattering spectroscopy (LEIS) /11,12/, field-ion microscopy /13/ etc. it is possible to investigate the surface composition of alloys in great detail. In Fig. 1.2 we show a typical experimental measurement of surface concentration of $\text{Cu}_x\text{Ni}_{4-x}$

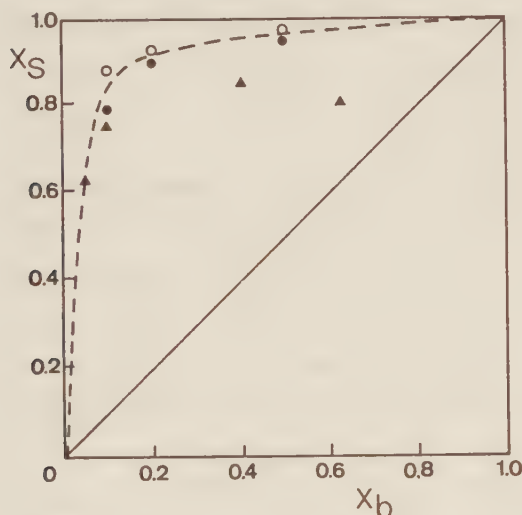


Fig. 1.2: Surface concentration x_s of Cu as a function of its bulk concentration x_b in $\text{Cu}_x\text{Ni}_{4-x}$ alloy. Closed and open circles correspond to temperatures 400°C and 500°C (Ref. 12); triangles are from the work by Sinfelt et al. /8/.

alloy as a function of its bulk concentration, at different temperatures. Clearly, deviation of the experimental curve (dashed

line) from no-segregation curve (full line) indicates a strong segregation of Cu-atoms at the surface. Recently /14/, surface composition is measured at different crystal faces of single crystal Cu-Ni alloys, which indicates that the segregation is slightly more in more opened (100) surface in comparison to the close-packed (111) surface. In addition to the abovementioned techniques a new tool to measure surface composition is recently invented, in which the heat of segregation of alloys is measured directly from the surface core-level shift (SCLS) of one element in the alloy. This measurement is based on the principle of equivalent core approximation /15/ and can be applied to the alloys whose components are neighbors in the periodic table (e.g. Cu-Ni). This kind of measurements have motivated further theoretical /16-19/ and experimental /20/ studies of surface core-level shifts in alloys, in connection with surface segregation.

Alloy catalysts normally used in technical applications are in the form of small particles (clusters) supported on silica substrate /5,21/. The metal dispersion, expressed as the ratio of surface metal atoms to total metal atoms, is in the range of 0.5 - 1 in these particles. The catalytic properties of these bimetallic cluster catalysts are governed largely by the geometry and chemical composition of their surface. Segregation of one of the constituents to the surface of the catalyst particle has a direct effect on its catalytic activity. The effect of cluster size on the segregation property has been experimentally studied by Sinfelt et al./6/ for ruthenium-copper and osmium-copper alloys. In bulk or in samples in the form of large aggregates, these alloys exhibit no miscibility in the whole concentration range /22/ with a very strong segregation tendency of copper on the surface. But in smaller samples, with

dispersion ranging from 0.5 to ~ 1 , Ru-Cu and Os-Cu alloys are found to be miscible with a moderate segregation of Cu on the surface. Sinfelt et al. [6] have used hydrogen chemisorption and ethane hydrogenolysis as probes and measured the relative chemical activity of the chemical reaction on supported clusters of Ru-Cu (Fig. 1.3). These measurements show that in highly dispersed samples of Ru-Cu, the relative specific activity of ethane hydrogenolysis decreases at a

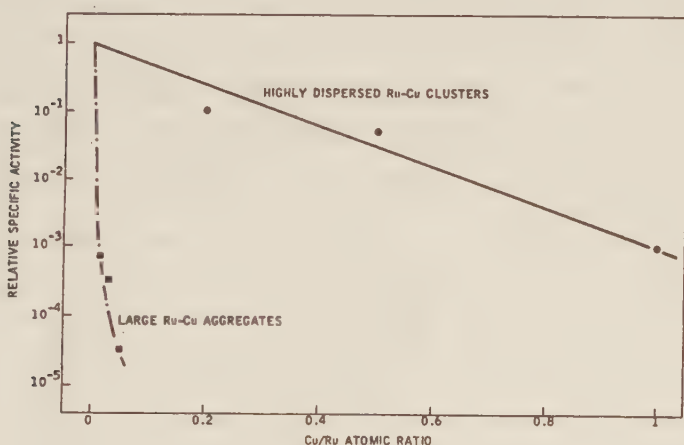


Fig. 1.3: Relative specific activity of ethane hydrogenolysis reaction on Ru-Cu bimetallic clusters as a function of Cu-concentration. (From Ref. 6)

much slower rate, with increasing copper concentration, compared to that in larger Ru-Cu aggregates. The very rapid decrease of the relative activity with Cu-concentration for larger aggregates indicates that the surface is completely enriched by Cu, whereas in small clusters the Cu segregation to the surface is moderate. Similar results were also obtained for Os-Cu alloy clusters. These measurements provide a motivation to study the effect of sample size on the surface segregation behavior in cluster alloys.

It is well known that the binding energies of gas atoms and molecules on transition-metals vary from element to element /23/. This happens due to different electronic structure and band-filling of the d-band of metals. One should therefore expect that chemisorption of gases may cause an atom exchange between surface and its neighborhood (bulk), thereby changing the surface composition of the alloy surface. This problem has not yet been extensively studied experimentally, firstly due to experimental difficulties in measuring surface concentration of the substrate alloy in presence of adsorbate atoms, and secondly due to the low mobility rate of the substrate atoms at experimental temperatures (upto about 400 K, above which desorption takes place). However, there exists a few measurements on

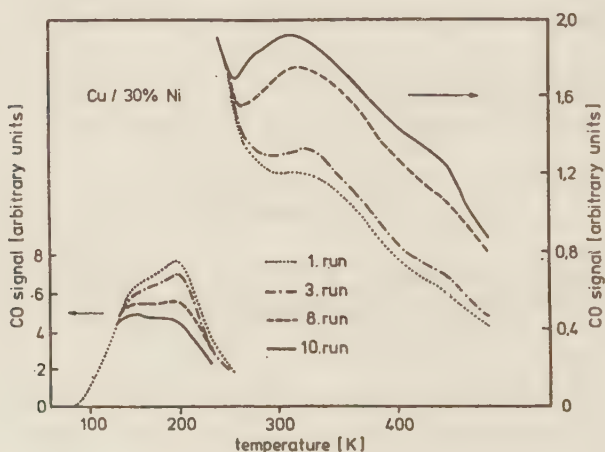


Fig. 1.4: Repetitive CO flash desorption traces from Cu rich surface of a Cu-Ni alloy. (Ref. /25/)

sample likes Cu-Ni /24-27/ and Au-Ni /28,29/ alloy surfaces which indicate that exposures of carbon monoxide and oxygen on these surfaces may change the segregating elements on these surfaces. These

alloys are expected to show similar behavior with respect to gas adsorption, as Cu and Au are both elements of group I in the periodic table and have same valence electron configuration. Furthermore, the adsorption energies of carbon monoxide, oxygen and hydrogen on Au, and of carbon monoxide and hydrogen on Cu are considerably lower than those for Ni. The flash-desorption measurements by Yu et al. /24/ and Harberts et al. /25/ show that with increasing temperature the CO desorption peak shifts from Cu to Ni (Fig. 1.4), indicating that the surface gets more richer in Ni in presence of CO. Similar studies were done by Burton et al. /28/ on Au-Ni (111) single-crystal surface. These experiments were carried out above room temperature and the adsorption profiles show only the peak representative of Ni. This peak decreases in intensity with increasing concentration of Au. However due to nonlinear behavior of the decrease in the amount of CO with increasing Au concentration, determination of surface concentration was not possible. Experiments with oxygen exposure /26/ on Cu-Ni surface are not easily interpretable, owing to the oxide formation of surface nickel and copper, but they also indicate the tendency of increasing Ni concentration.

These experimental investigations provide a motivation to study the effect of chemisorption on surface segregation at alloy surfaces. It is interesting to mention that this problem can be treated as a special case of the more general problems of segregation at the interfaces of ternary alloys. In chapter 3 we will calculate the effects of chemisorption, bulk absorption and sample size on the surface segregation property of alloys.

In the last part of the earlier section we discussed about the problem of mixing of gas atoms on alloy surfaces and its consequences like induced surface segregation. Here we shall look into the microscopic mechanism of mixing (chemical reaction) of oxygen atoms on nickel surface. It is well known that oxygen is dissociatively adsorbed on Ni-surfaces /30-33/, the binding energy of oxygen on polycrystalline Ni-surface being $\sim 4-5$ eV. On crystalline Ni-surfaces, as shown by recent low energy electron diffraction (LEED) measurements, oxygen atoms form an ordered structure at low coverages which is stable upto a temperature of 400 K. At higher coverages ($\theta > 0.5$ for (100) surface and $\theta > 0.35$ for (111) surface) nickel-oxide formation takes place, which passes through two stages /34-36/ -- (a) an initial fast oxidation stage to a depth of 2-3 atomic layers and (b) a much slower oxide thickening stage. However, the nucleation of oxide is drastically affected due to temperature and perfection of Ni-surface /36/. In table 1.1 we summarize the different oxygen phases on various Ni surfaces as observed at near room temperature.

X-ray photoelectron spectroscopic (XPS) measurements on O(1s) intensities, supported with LEED in ultra-high vacuum conditions /37,38/, indicate that the rate of initial oxide growth is very rapid at low temperatures (77 K) than at higher temperature (~ 300 K) (Fig. 1.5). This can be explained as follows :

(i) At low temperature, mobility of the chemisorbed oxygen atoms is inhibited and ordered structures of oxygen atoms are not formed. So it is possible that at very low coverages oxygen atoms form a local coverage greater than half monolayer, thereby starting the oxide

nucleation.

(ii) At high temperature (300 K), at first p(2x2) structure forms which converts into a c(2x2) structure at higher coverage. Upon further increment of oxygen exposure, oxygen atoms form a local coverage greater than half monolayer and oxide formation starts.

Ni-surface	Oxygen phases	Coverage
(100)	p(2x2)	0.25
	c(2x2)	0.5
	NiO	> 0.5
(111)	(2x2)	0.25
	($\sqrt{3} \times \sqrt{3}$) R 30	0.33
	NiO	> 0.35 - 0.4
(110)	(3x1)	
	(2x1)	
	NiO	

Table 1.1: Table summarizing the chemisorbed oxygen phases on Ni-surfaces at near room temperature.

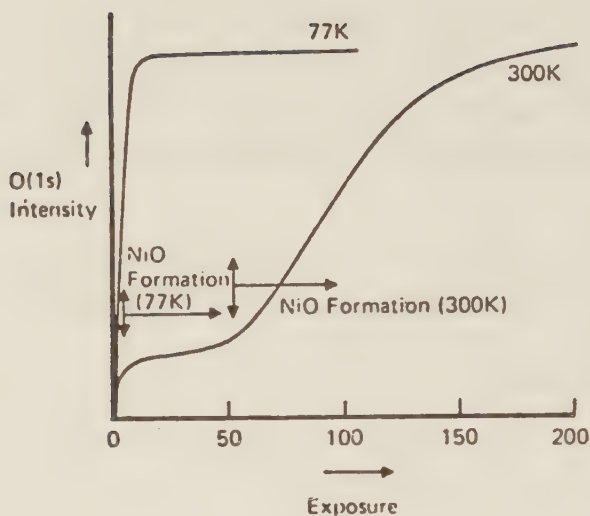


Fig. 1.5: Chemisorbed oxygen uptake curves for Ni(100) at different temperatures. (From ref. /37/)

From these experimental studies one may conclude that a local coverage greater than half monolayer is essential for oxide nucleation at clean surfaces. The mechanism of oxidation can be understood in a way, that the binding energy of oxygen atom decreases rapidly with increasing coverage beyond half monolayer. However, the binding energy of O-atoms in the bulk of Ni (between surface and first few layers) may be independent of the oxygen coverage and if it is larger than that of a surface O-atom at $\theta = 1$, then one can expect that beyond the critical coverage θ_c O-atoms will prefer to go into the bulk. So one can think of oxidation process, in which O-atoms face an energy barrier. This barrier height depends strongly on the

perfection of Ni-surface and on temperature. In chapter 4 we present theoretical models to calculate the binding energy of oxygen atom on nickel surface at various coverages and will interpret the formation of overlayer structures and oxide formation of nickel surface.

In conclusion, the problems dealt in this thesis are as follows. In chapter 2, we present an electronic theory of surface segregation which can be applied to alloys of transition metals and noble metals, and apply this theory to calculate surface composition of Cu-Ni alloy. Furthermore, we present a theory for calculating the surface core-level shift and its relationship to surface segregation for alloys. In chapter 3, effects of chemisorption, bulk absorption and the size of the sample on the surface segregation behavior of alloys will be studied. Finally, in chapter 4, gas-surface interaction will be studied in detail for chemisorbed oxygen and sulfur on Ni(100) surface for a detail understanding of the coverage dependent chemisorption and subsequent compound formation on nickel surfaces. In appendix A, expression for the Green's function at the surface of a binary alloy, derived in a Bethe-lattice approximation, is given. This is used to calculate the local density-of-states (LDOS) used in chapter 2. In appendix B, we present an account of the recursion method for calculating the LDOS more accurately, used in chapter 4; and in appendix C, expression for the change in Coulomb and exchange-correlation energy due to chemisorption is given.

2. ELECTRONIC THEORY FOR THE SURFACE SEGREGATION AND SURFACE CORE-LEVEL-SHIFT IN TRANSITION METAL ALLOY

2.1 ELECTRONIC THEORY OF SURFACE SEGREGATION IN TRANSITION- METAL ALLOY

As stated in Chapter I, the surface composition of transition-metal alloys plays a determining role in the catalytic and related properties of these alloys. In recent years surface composition of metal alloys are studied intensively. Particular attention has been given to investigate the surfaces of Cu-Ni alloys /9-13/, and a strong segregation of Cu-atoms has been reported. Very recently extensive measurements /14/ show that (100)-surface of Cu-Ni alloy shows an enhanced Cu-segregation than on (111)-surface.

Several theories of surface segregation in alloys have been proposed. Among the phenomenological theories, the pair-bond models /39-42/ for the interatomic interactions are mostly used. This model shows, the constituent having the lower heat of vaporization segregates to the surface. However, it has been recently shown /43-47/ that using surface energies to describe surface segregation gives a better agreement for a large number of systems including those with components of appreciably different molar volumes. Theories

/48,49/ taking into account both bond breaking and volume effects and including long-range and short-range atomic order /50,51/ have also been presented.

Microscopic electronic theories of segregation /52-58/ presented so far use a tight-binding type model to describe the valence band of the metal. In earlier theories of this kind /52/, the electron-correlation effects have been neglected. Recent theories taking account of electron-correlation effects, by solving the Hamiltonian in the Hartree-Fock approximation, find a good agreement with the measured segregation for noble-metal /54/ and simple-metal /55/ alloys. Recently, tight-binding type theories /56-58/ are also presented to calculate surface segregation of dilute transition-metal impurities in transition-metal and noble-metal hosts. In this chapter we present a tight-binding type model to describe the d-electrons for transition-metal alloys, taking electron correlation effects into account, and apply this theory to calculate surface segregation in $\text{Cu}_x\text{-Ni}_{1-x}$ alloy for entire concentration range. Our calculation is based on determining the free energy as a function of the alloy concentration, from which, after minimizing it with respect to the alloy concentration, we obtain the equilibrium surface concentration. The segregation for (100) and (111) surfaces of Cu-Ni alloy, as well as the temperature dependence of surface segregation is calculated and compared with existing experimental results. We also show that the effect of surface segregation is clearly reflected in the surface electronic density-of-states (DOS). Later, in this chapter, we present an electronic theory for calculating the surface core level binding energy shift (SCLS) in alloys and apply this to $\text{Cu}_x\text{Ni}_{1-x}$ alloy surfaces. Results of our calculations will be discussed in the

last section.

2.1.1 MODEL

The equilibrium concentration at any plane parallel to the surface of $A_X B_{1-X}$ alloy is calculated by minimizing the total free energy,

$$F(x_1, x_2, \dots) = U(x_1, x_2, \dots) - T S(x_1, x_2, \dots) \quad (2.1)$$

of the crystal with respect to the concentration $x_1, x_2, \dots$ etc. of the surface, second etc. layers respectively. We consider that the crystal consists of a set of planes parallel to the surface and assume the alloy to be random (i.e. at a temperature higher above the order-disorder transition temperature). The internal energy U can be expressed as a sum of the contributions from individual layers as,

$$U(x_1, x_2, \dots) = \sum_{\lambda=1}^{\infty} U_{\lambda}(x_1, x_2, \dots) \quad (2.2)$$

and the configurational entropy of the random alloy is given by,

$$S = -k_B \sum_{\lambda=1}^{\infty} \left[x_{\lambda} \ln x_{\lambda} + (1-x_{\lambda}) \ln (1-x_{\lambda}) \right] \quad (2.3)$$

the conservation of total number of A and B atoms and electrons are given by the constraints,

$$\sum_{\lambda=1}^{\infty} x_{\lambda} = \text{const.}$$

and

$$\sum_{\lambda=1}^{\infty} \langle n_{\lambda} \rangle = \text{const.}$$

Now, including these constraints in the free energy expression (Eq. 2.1) using Lagrange multipliers, we obtain the grand free energy,

$$\begin{aligned} \mathcal{F}(x_1, x_2, \dots) &= F(x_1, x_2, \dots) \\ &- \mu \sum_{\lambda=1}^{\infty} x_{\lambda} - \nu \sum_{\lambda=1}^{\infty} \langle n_{\lambda} \rangle \end{aligned} \quad (2.4)$$

The equilibrium concentration in the i -th layer is given by $\partial \mathcal{F} / \partial x_i = 0$. The lagrange multipliers μ and ν are related to the bulk parameters : chemical potential and Fermi energy, respectively and are given by,

$$\mu = \frac{\partial F}{\partial x_b}, \quad \nu = \frac{\partial F}{\partial \langle n_{\lambda} \rangle} \equiv \epsilon_F \quad (2.5)$$

Now in order to calculate the internal energy U , we use the tight-binding Hartree-Hamiltonian with intratomic electron-electron Coulomb interaction U_e . We take only the d-band into account, as the electronic density-of-states (DOS) of $\text{Cu}_x\text{Ni}_{1-x}$ alloy system at the Fermi level is mainly of the d-character [59]. The Hamiltonian is written as,

$$H = \sum_{i,\sigma} \epsilon_{i\sigma} n_{i\sigma} + \sum_{\substack{i \neq j \\ \sigma}} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} \quad (2.6)$$

where,

$$\epsilon_{i\sigma} = \epsilon_{i\sigma}^0 + U_e \langle n_{i,-\sigma} \rangle \quad (2.7)$$

Here, $c_{i\sigma}^\dagger$ and $c_{i\sigma}$ are usual creation and destruction operators for electron with spin σ in the Wannier state at site i , occupied by $\langle n_{i\sigma} \rangle$ electrons. $\epsilon_{i\sigma}^0$ and t_{ij} are the single site energy and hopping integral between nearest neighbor sites, respectively. The hopping integral t_{ij} can have values t_{AA} , t_{BB} and t_{AB} depending on the type of atoms on sites i and j .

The local density-of-states (LDOS) for λ -th plane is determined from one-particle Green's function $G_{ii,\sigma}(E)$ as,

$$\rho_\lambda^i(E) = -\pi^{-1} \text{Im} \sum_\sigma G_{ii,\sigma}(E), \quad i \equiv A, B \quad (2.8)$$

The average LDOS in the λ -th layer is given by,

$$\rho_\lambda(E) = x_\lambda \rho_\lambda^A(E) + (1 - x_\lambda) \rho_\lambda^B(E) \quad (2.9)$$

The average number of electrons per site in the λ -th layer is given as,

$$\langle n_\lambda \rangle = \int_{-\infty}^{\epsilon_F} \rho_\lambda(E) dE \quad (2.10)$$

and the internal energy of an atom in the λ -th layer is,

$$U_{\lambda}(x_1, x_2, \dots) = \int_{-\infty}^{\epsilon_F} E \rho_{\lambda}(E) dE - E_{ee}^{\lambda} \quad (2.11)$$

Here, E_{ee}^{λ} is the correction term in the energy per atom in the λ -th layer, due to Hartree-Fock approximation and is given for an atom at site i by,

$$E_{ee}^{\lambda}(i) = \frac{1}{2} \sum_{\sigma} (\epsilon_{i\sigma} - \epsilon_{i\sigma}^0) \langle n_{i\sigma} \rangle \quad (2.12)$$

The diagonal Green's function $G_{ii,\sigma}(E)$ is evaluated within the cluster-Bethe-lattice model. In this method one substitutes the infinite periodic lattice by an infinite system of connected atoms, with the same coordination number Z as in the lattice under consideration, but neglecting close rings of bonds. This lattice has the property, that in the bulk of binary alloy, the one particle Green's function is written in terms of a set of four transfer functions.

In order to describe the surface of the binary alloy we use the mixed Bethe-lattice model, in which a surface atom is assumed to be connected to Z_0 (number of nearest neighbors in surface plane) surface atoms, and Z_1 (number of nearest neighbors between two adjacent planes) bulk atoms. The number of nearest neighbors in the bulk being $Z = Z_0 + 2Z_1$. We need in this case three other sets of transfer functions depending upon whether the connection between atoms is made between two surface atoms, between a surface and a bulk atom or

between a bulk and a surface atom. Some details of cluster-Bethe-lattice model is presented in Appendix A, where we also give expressions for diagonal Green's functions for a bulk and a surface atom. It should be noted that this model can be easily extended to calculate the local Green's function at any arbitrary layer, by introducing proper transfer functions.

2.1.2 Calculation of Segregation in Cu-Ni alloy

The essential parameters for the calculation of surface segregation in the $\text{Cu}_x\text{Ni}_{1-x}$ alloy are the band-widths of the pure elements of the alloy, the mean energies of the d-band and the number of the d-electrons. In Table 1 we summarize the input parameters used in the calculation.

Parameter	Value
d-band width (Cu)	3.34 eV
d-band width (Ni)	4.3 eV
$\epsilon_{\text{Ni}} - \epsilon_{\text{Cu}}$	1.8 eV
$n_d(\text{Cu})$	10
$n_d(\text{Ni})$	9.4
U_e	2 eV

Table 2.1 : Essential parameters used in the calculation of electronic structure of Cu-Ni alloy. Values are from ref. /19/.

The calculations were done in the following steps. At first the Green's functions for bulk are solved and the local density-of-states are calculated. Then Eqs. (2.7) and (2.10) are solved self-consistently, in order to include electron correlations into account. Self-consistency was achieved within an accuracy of 0.0001 e of charge. Then using Eqs. (2.1), (2.3) and (2.11) total free energy for bulk was calculated as a function of bulk concentration and finally using relations (2.5), the bulk parameters μ and ν were calculated. Then the calculation for the surface was carried on, taking the bulk parameters as input. The self consistency for the surface potential was achieved also within an accuracy of 0.0001 e of charge, and finally the grand function $\mathcal{F}(x_1, x_2, \dots)$ was calculated for given surface and bulk concentration. Then using standard routine, $\mathcal{F}(x_1, x_2, \dots)$ was minimized and equilibrium surface concentration was calculated at different temperatures. Calculations were performed for both (111) and (100) surfaces of $\text{Cu}_x\text{Ni}_{1-x}$ alloys.

In Fig 2.1 we present results for the surface concentration X of Cu on a (111) surface for two different temperatures 400°C and 500°C. In Fig 2.2 we compare the surface segregation results for $U_{\bar{e}}=0$ with that of $U_{\bar{e}}=2$. This shows the importance of electron-electron Coulomb interaction in the theory. In Fig 2.3 we show the temperature dependence of the surface Cu-concentration for a fixed value of bulk concentration. In Fig 2.4 we compare the surface concentrations for (111) and (100) surfaces at 400°C.

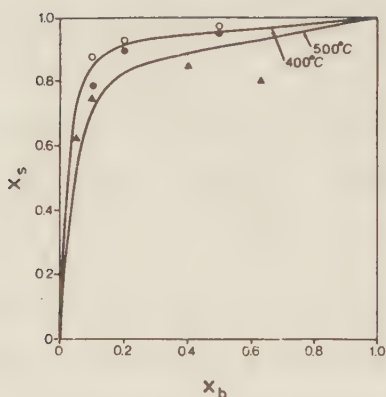


Fig. 2.1 Surface concentration x_s of Cu as a function of its bulk concentration x_b on (111) surface of $\text{Cu}_x\text{Ni}_{1-x}$ alloy at 400°C and 500°C. Experimental values refer to Brongersma et al./12/. Open circles : at 400°C, Full circles : at 500°C; and Sinfelt /8/ (triangles).

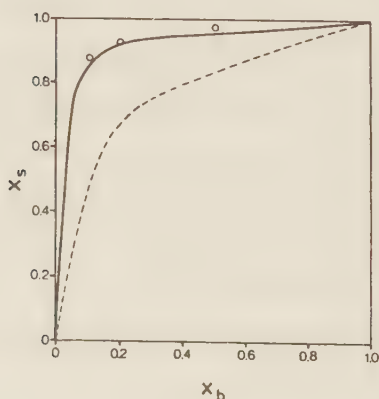


Fig. 2.2 Surface concentration x_s of Cu as a function of its bulk concentration x_b on (111) surface of $\text{Cu}_x\text{Ni}_{1-x}$ alloy at 400°C. The full curve refers to Coulomb interaction $U_2 = 2 \text{ eV}$ and dashed curve to $U_2 = 0$.

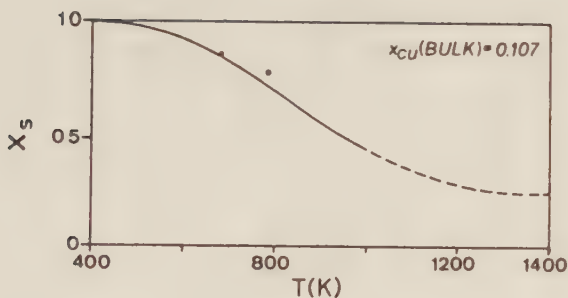


Fig. 2.3 Surface concentration x_s of Cu on (111) surface of $\text{Cu}_x\text{Ni}_{1-x}$ alloy with $x_b = 0.107$, as function of temperature. Experimental points are taken from Brongersma et al. /12/.

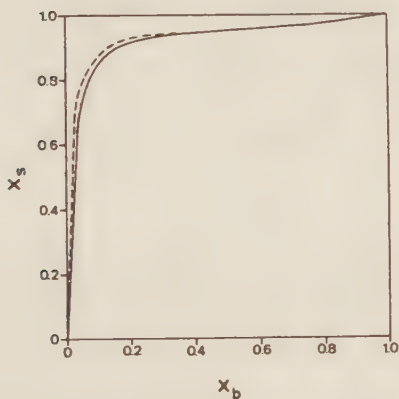


Fig. 2.4 Surface concentration of Cu as a function of its bulk concentration at 400°C for (111) surface (full line), and for (100) surface (dashed line).

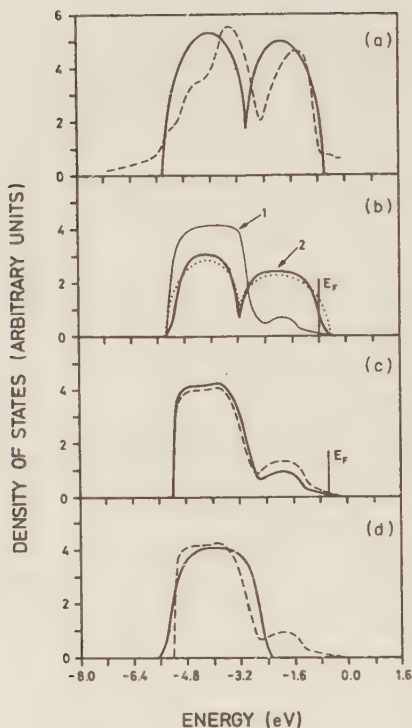


Fig. 2.5 : Various results for the electronic density-of-states at (111) surface of CuNi_{1-x} alloy. (a) Total DOS in bulk for $x_b = 0.62$ (full curve). Dashed curve refers to the CPA calculation by Stocks et al. /59/, again for $x_b = 0.62$. (b) Average bulk DOS at $x_b = 0.5$ (dotted curve). Curves 1 and 2 refer to the DOS at the surface for $x_s = 0.95$ and $x_s = 0.5$, respectively. Note, $x_s = 0.95$ is the calculated surface concentration for $x_b = 0.5$. (c) Average surface DOS with $x_b = 0.2$ and $x_s = 0.91$ (full curve) and $x_s = 0.83$ (dashed curve). These two surface concentrations are calculated x_s for $x_b = 0.2$ at 400°C and 500°C , respectively. (d) Comparison of DOS at surface for $x_b = 0.2$, $x_s = 0.91$ (dashed curve) with that of pure Cu (full curve).

In Fig. 2.5(a) we show the total bulk DOS for $x_b = 0.62$. For comparison results are also shown for $x_b = 0.62$ as obtained by Stocks et al./59/ using coherent-potential-approximation (CPA). The detail structures of DOS are not present in our calculation, but the main features compare well. In Fig 2.5(b) we illustrate how the surface segregation affects the surface-DOS. Instead of curve 2, which would give the DOS in the absence of surface segregation, one obtains a DOS shown by curve 1 as a result of segregation. In Fig 2.5(c) we show the surface-DOS for two different surface concentrations. The full curve refers to $x_s=0.91$ and the dashed curve to $x_s=0.83$, with corresponding bulk concentration 0.2. These two different surface concentrations correspond to two different temperatures 400°C and 500°C respectively. In Fig 2.5(d) we compare the surface-DOS for $x_s=0.2$, $x_s=0.91$ (dashed curve) with that of pure Cu (full curve).

2.2 THEORY OF SURFACE-CORE-LEVEL-SHIFT FOR ALLOY AND ITS RELATIONSHIP TO SEGREGATION

As the chemical composition and coordination (number of neighboring atoms) are different from that of in the bulk of an alloy, surface atoms experience a different potential than bulk atoms. Therefore, in general, the core-level binding energy is different for surface and bulk atoms. Recently, surface core-level binding-energy-shifts (SCLS) have been measured using X-Ray photoelectron spectroscopy (XPS) for metals /61/ and alloys /20/. It has been pointed out that the surface-core-level-binding-energy-shifts for alloys give adequate information about the heat of segregation /17-19/ and alloy formation energies /17/.

In the XPS measurement of the core-level-binding-energy, a core-level is ionized from a particular atomic site of the solid. Assuming that the site from which the core electron is ejected will become totally screened by the surrounding conduction electrons, it is possible to write the core-level excitation energy as /15/,

$$E_{c,F}^b = -E_{coh}^b(Z^*) + E_{coh}^b(Z) + E_{c \rightarrow v} - E_{Z^*}^{imp}(Z) \quad (2.13)$$

Here Z^* represents the core-excited bulk atom (with atomic number Z), $E_{c \rightarrow v}$ is the excitation energy of the core electron c into the valence band v , and E_{coh}^b is the bulk cohesive energy. $E_{Z^*}^{imp}(Z)$ is the heat of solution of the impurity Z^* in metal Z . Using the ansatz of Johansson and Martensson /15/, that a core with one electron removed from a deep lying inner shell can be replaced quite accurately by the of the $(Z+1)$ -atom, Eq (2.13) can be simplified as,

$$E_{c,F}^b = -E_{coh}^b(Z+1) + E_{coh}^b(Z) + E_{c \rightarrow v} - E_{Z+1}^{imp}(Z) \quad (2.14)$$

Now, in the case of alloy A_xB_{1-x} , if we assume the core-excitation process of an A-atom in the bulk, a similar expression for the core-level-binding-energy for the A-component is written as,

$$E_{c,F}^b(A, A_xB_{1-x}) = -E_{coh}^b(A^*) + E_{coh}^b(A, A_xB_{1-x}) + E_{c \rightarrow v} - E_{A^*}^{imp}(A_xB_{1-x}) \quad (2.15)$$

where $E_{coh}^b(A, A_xB_{1-x})$ is the cohesive energy of A in the bulk of the alloy. In writing eqs. (2.13) - (2.15), the core-level excitation energy $E_{c,F}^b$ is written as the difference of the total energies in final and initial states of the system. This can be best described by a Born-Haber cycle (Fig. 2.6) for the alloy, in analogy to that of a metal [15]. In order to core-excite an atom A, in the first stage, the atom A is removed from the alloy A_xB_{1-x} . This process costs the cohesive energy $E_{coh}^b(A, A_xB_{1-x})$ of A in alloy A_xB_{1-x} . Then this atom A, with atomic number Z, is core-ionized (with ionization energy E_C^A). The core-ionized state of the atom A(Z) is equivalent to the ion $A^*(Z+1)$, which is then neutralised to the atomic state. In this process the ionization energy $I_{A^*}^{Z+1}$ will be freed. Next, we bring together a macroscopic number of such $A^*(Z+1)$ atoms to form a solid, which is then dissolved into the alloy A_xB_{1-x} in very dilute quantity. The energy freed in the last two steps are cohesive energy $E_{coh}(A^*)$ of metal $A^*(Z+1)$ and the heat of mixing $E_{A^*}^{imp}(A_xB_{1-x})$ of the impurity $A^*(Z+1)$ in the alloy. Eq. (2.15) follows from completing the cycle, where $E_{c \rightarrow v} = E_C^A - I_{A^*}^{Z+1}$ is the excitation energy of the core electron into the valence band.

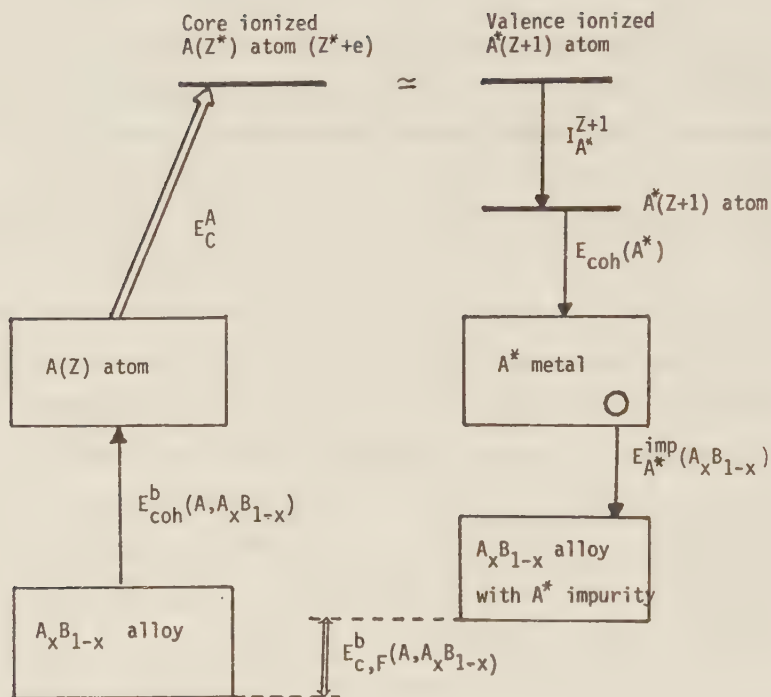


Fig. 2.6 : Born-Haber cycle for the calculation of core-level binding energy $E_{C,F}^b(A, A_x B_{1-x})$ in alloy, which is analogous to that in metals^{1/15/}.

Now, the eq. (2.15) can be rewritten as,

$$E_{c,F}^b(A, A_x B_{1-x}) = -E_{coh}^b(A^*, A_x B_{1-x}) + E_{coh}^b(A, A_x B_{1-x}) + E_{c \rightarrow v}^{(A)} \quad (2.16)$$

where,

$$-E_{coh}^b(A^*, A_x B_{1-x}) = -E_{coh}^b(A^*) - E_{A^*}^{imp}(A_x B_{1-x})$$

Similarly for the B-atom,

$$E_{c,F}^b(B, A_x B_{1-x}) = -E_{coh}^b(B^*, A_x B_{1-x}) + E_{coh}^b(B, A_x B_{1-x}) + E_{c \rightarrow v}^{(B)} \quad (2.17)$$

Similarly, the core-level binding energies for the surface atoms are written as,

$$E_{c,F}^s(A, A_x B_{1-x}) = -E_{coh}^s(A^*, A_x B_{1-x}) + E_{coh}^s(A, A_x B_{1-x}) + E_{c \rightarrow v}^{(A)} \quad (2.18)$$

and,

$$E_{c,F}^s(B, A_x B_{1-x}) = -E_{coh}^s(B^*, A_x B_{1-x}) + E_{coh}^s(B, A_x B_{1-x}) + E_{c \rightarrow v}^{(B)} \quad (2.19)$$

The superscripts b and s in Eqs (2.15)-(2.19) refer to bulk and surface respectively. The surface-core-level-binding-energy-shift of A-atom is written as,

$$\begin{aligned} \Delta_c^s(A) &= E_{c,F}^s(A, A_x B_{1-x}) - E_{c,F}^b(A, A_x B_{1-x}) \\ &= E_{coh}^b(A^*, A_x B_{1-x}) - E_{coh}^s(A^*, A_x B_{1-x}) \\ &\quad - \{ E_{coh}^b(A, A_x B_{1-x}) - E_{coh}^s(A, A_x B_{1-x}) \} \end{aligned}$$

$$\text{i.e., } \Delta_c^S(A) = E^S(A^*, A_x B_{1-x}) - E^S(A, A_x B_{1-x}) \quad (2.20)$$

where, $E^S(A, A_x B_{1-x})$ denotes the surface enthalpy (difference in energy of an atom in bulk and in the surface) of A-atom in the alloy $A_x B_{1-x}$.

The SCLS for a B-atom can be written in an analogous way as,

$$\Delta_c^S(B) = E^S(B^*, A_x B_{1-x}) - E^S(B, A_x B_{1-x}) \quad (2.21)$$

If A and B are the neighboring elements in the periodic table, then $A = B^*$ (which is the case for $\text{Cu}_x\text{Ni}_{1-x}$ alloy). Therefore, Eq (2.21) can be rewritten as,

$$\Delta_c^S(B) = E^S(A, A_x B_{1-x}) - E^S(B, A_x B_{1-x}) \quad (2.22)$$

It is easy to see that expression (2.22) represents the heat of segregation of B-element in the alloy $A_x B_{1-x}$. The first term in Eq (2.22) represents the energy needed in transferring one A-atom from bulk to the surface, whereas, the second term represents the energy gain in transferring a B-atom from surface to the bulk. Therefore, if $\Delta_c^S(B)$ is negative one expects a surface enrichment of A, and if $\Delta_c^S(B)$ is positive then surface enrichment of B will occur.

2.2.1 Calculation of the SCLS of $\text{Cu}_x\text{Ni}_{1-x}$ alloy

As shown in Eq (2.22) the surface-core-level-shift of the element-B is given as the difference between the surface enthalpies of the components A and B in $A_x B_{1-x}$ alloy. In terms of the local density-of-states $\rho_s^i(b)$ at surface (bulk), the surface enthalpy can be written as,

$$E^S(A, A_x B_{1-x}) = \int_{-\infty}^{\epsilon_F} (E - \epsilon_A^S) \rho_s^A(E) dE - \int_{-\infty}^{\epsilon_F} (E - \epsilon_A^b) \rho_b^A(E) dE - (E_{ee}^S(A) - E_{ee}^b(A)) \quad (2.23)$$

Here, $E_{ee}(A)$ denotes the correction term in energy for A-atom due to the Hartree-Fock approximation, given by Eq (2.12). Therefore Eq (2.22) can be written as,

$$\begin{aligned} \Delta_c^S(B) &= \int_{-\infty}^{\epsilon_F} E (\Delta \rho^A(E) - \Delta \rho^B(E)) dE \\ &\quad - (n_A^S \epsilon_A^S - n_A^b \epsilon_A^b - n_B^S \epsilon_b^S + n_B^b \epsilon_B^b) \\ &\quad - (E_{ee}^S(A) - E_{ee}^b(A) - E_{ee}^S(B) + E_{ee}^b(B)) \quad (2.24) \end{aligned}$$

where,

$$\Delta \rho^i(E) = \rho_s^i(E) - \rho_b^i(E)$$

and,

$$n_i^{s(b)} = \int_{-\infty}^{\epsilon_F} \rho_{s(b)}^i(E) dE$$

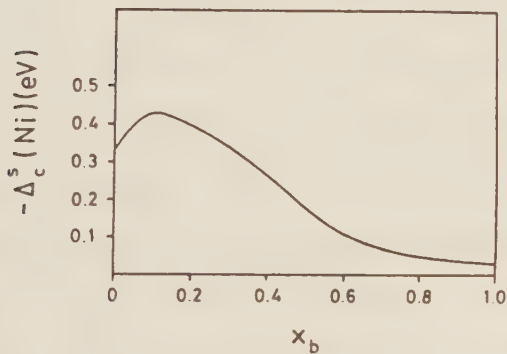


Fig. 2.7 The surface core-level shift for Ni, $\Delta_c^S(\text{Ni})$, as a function of bulk Cu concentration.

The above expression is used to calculate the SCLS for Ni in $\text{Cu}_x\text{Ni}_{1-x}$ alloy for (111) surface and shown in Fig 2.7 for $T=400^\circ\text{C}$. A similar expression for SCLS of Cu can also be written, but in the present formulation it is not possible to calculate, because one needs the surface enthalpy of Zn (next higher element of Cu in the periodic table), in $\text{Cu}_x\text{Ni}_{1-x}$ alloy.

2.3 DISCUSSION OF THE RESULTS

In our calculation of the surface segregation we have assumed only surface concentration of the alloy to be different from its bulk value (the monolayer model). From experiments /10-12/ and calculations based on bond breaking model, the concentrations in the second, third ... etc. layers were found to be very nearly equal to the bulk value, and therefore the monolayer model is a good approximation for Cu-Ni alloy.

As can be seen from Fig. 2.1, our surface segregation results are in good agreement with the results obtained by low energy ion scattering experiment /12/, which precisely measures the surface concentration. The results in Fig. 2.2 indicate the importance of electron correlation in segregation. We find that for $U_e \neq 0$, surface segregation of Cu is enhanced. A similar effect has been observed in earlier calculation /54/. Results for temperature dependence of surface concentration (Fig. 2.3) indicate that with increasing temperature the surface Cu-concentration decreases and approaches the bulk value. This behavior is expected from alloy thermodynamics. Our results shown in Fig. 2.4 indicate slight enhancement of Cu surface segregation on the more opened (100) surface as compared to on (111)

surface, a fact which is observed experimentally /14/. From the results of DOS in Fig. 2.5 it is obvious that with increasing concentration the peak in the average DOS centered on Cu increases. Consequently, one expects strong Cu peaks in the energy distribution curves of photoelectron emitted from a Cu rich Cu-Ni alloy surface, as observed /60/. Fig. 2.5(c) illustrates that with increasing temperature the Cu peak will decrease, since the Cu concentration at the surface decreases. Fig. 2.5(d) shows that in case of very strong surface segregation of Cu, the average DOS at the surface looks almost similar to that of pure Cu.

In Fig. 2.7 results are shown for surface core level binding energy shift (SCLS) for Ni on (111) surface, calculated from eq. (2.24). Note, our calculated SCLS of about -0.4 eV at low Cu concentration agrees well with recent core level shift measurements /20/. Moreover, our results obtained from a self-consistent calculation show a similar trend as those obtained by Kumar et al. /18/ using a phenomenological model. For transition-metals, Desjonqueres et al. /62/ have explained the origin of the SCLS as a consequence of the atomic d-level shifts at the surface in order to preserve charge neutrality. In our calculation this shift $\Delta\epsilon_d$ in d-level is calculated self-consistently and we also noticed that the change in $\Delta\epsilon_c^s(\text{Ni})$ at the surface for Ni is similar to the curve shown in Fig. 2.7. For small bulk Cu concentration, a big shift is observed in the surface core level of Ni, which can be understood from the DOS curves shown in Fig. 2.5. In the bulk there will be large DOS near the Fermi energy, whereas at the surface, because of small Ni concentration, a small DOS will be observed at E_F . So, to preserve the charge neutrality, Ni level has to be shifted to higher energies.

As the bulk concentration increases, the shift reduces. This is because the surface DOS is expected to remain almost unchanged because of small variation in surface concentration, as the bulk concentration increases.

3. THEORY FOR THE CHEMISORPTION, ABSORPTION AND SAMPLE SIZE INDUCED CHANGES IN SURFACE SEGREGATION IN BINARY METAL ALLOYS

As pointed out in the introduction, there exists experimental evidence of the phenomena of chemisorbed induced segregation (CIS), owing to the fact that the chemisorption energies of gas atoms or molecules (e.g. hydrogen, oxygen, carbon monoxide etc.) are different on different metals. These experimental findings, though somewhat indirect and qualitative, provides a motivation for theoretical study of chemisorption induced segregation phenomena. In this chapter we provide a calculation of chemisorption induced segregation in various metal alloys and segregation due to absorption of hydrogen in Pd-Zr alloy. We also present an account of the size effect of the sample alloy on its segregation behaviour. The phenomena of chemisorption and absorption induced segregation can also be explained in the light of a more generalised problem of interfacial segregation occuring in the interface of an alloy $A_x B_{1-x}$ and a pure substance C. The atomic segregation at the interface is controlled by the heats of exchange $Q(A,C)$ and $Q(B,C)$. In the last section of this chapter expressions for the above quantities will be given and its relevance to other problems will be discussed.

3.1 CHEMISORPTION INDUCED SEGREGATION IN ALLOYS

We shall at first discuss the heat of segregation on a clean surface of a binary alloy and then extend it to the case when chemisorbed atoms or molecules are present. A major contribution to the driving force for segregation at the surface of alloys is the difference in the heats of vaporization or the surface energies of its pure constituents. For a monolayer regular solution model, the surface concentration x_s of solute A in the alloy $A_x B_{1-x}$ is given by,

$$\frac{x_s}{1 - x_s} = \frac{x}{1 - x} \exp(Q_{seg}/kT) \quad (3.1)$$

where Q_{seg} expresses the energy involved in exchanging a surface A-atom with a bulk B-atom. Now, as the exchange of A and B atoms will involve a heat of solution term to account for the modified environment of the exchanged atoms in the bulk and at the surface, the heat of segregation is written as /43/,

$$Q_{seg} = \frac{1}{3} \left[\Delta H_{sol}(A,B) - (\Delta H_{vap}^A - \Delta H_{vap}^B) \right] \quad (3.2)$$

In this expression $\Delta H_{sol}(A,B)$ is the heat of solution of the solute (A) in the solvent (B), $\Delta H_{vap}^{A(B)}$ represents the heat of vaporization of pure elements A(B) and the factor 1/3 arises due to the fact that on the average one third of the bulk bonds are broken on a clean alloy surface. Furthermore, there is some relaxation of the electron density distribution and the position of the atoms in the surface layer. Due to this, the fraction of surface area of a surface

atom in contact with the vacuum gets smaller than one third. Defining this relaxation factor by f , we get,

$$Q_{seg} = \frac{f}{3} \left[\Delta H_{sol}(A, B) - \Delta H_{vap}^A + \Delta H_{vap}^B \right] \quad (3.3)$$

From an analysis of surface energy values f is found to be 0.71 /43/.

The eq. (3.3) can be further generalised by writing ΔH_{vap} in terms of surface enthalpy. As shown by Miedema /63/, the heat of vaporization and surface enthalpy (γ) times molar surface area (σ) follow the relation, $\Delta H_{vap} = \kappa(\gamma \cdot \sigma)$. The constant κ is nearly same for metals /63,64/, its average value being $\sim 5.6 \times 10^8$. Therefore eq. (3.3) can be rewritten as,

$$Q_{seg} = \frac{1}{3} \left[f \Delta H_{sol}(A, B) - g(\gamma_A - \gamma_B) \sigma_A \right] \quad (3.4)$$

where $g = 4 \times 10^8$, and it is assumed that the molar volumes of A- and B-atoms are nearly same.

We use eq. (3.4) to calculate the segregation in 27 alloys and get excellent agreement for the segregating elements, except for Cr-Pt and Fe-Pt alloys. Now we shall extend the expression for Q_{seg} for chemisorbed surfaces.

In case of chemisorption of gases on alloy surfaces one is confronted with a three-component system for the surface layer. Assuming adsorption of a single layer of gas atoms, the physical situation is illustrated in Fig. 3.1

As the chemisorption energy of the adsorbates vary from metal to metal /23,65/, the segregation enthalpy will be modified in the presence of adsorbates. Denoting the chemisorption energy by $E_{A(B)}$ for the adsorbate on pure A(B) metals, the segregation enthalpy for chemisorbed surface can be given as /66/,

$$Q_{seg}^{Chem} = Q_{seg} + (E_A - E_B) \theta \quad (3.5)$$

where θ is the adsorbate coverage ($\theta = 1$ means monolayer coverage).

Element	Chemisorption bond energy (eV) for adsorbates:		
	H	O	CO
Ag		3.471 /a/	0.29 /a/
Au			0.394 /b/
Cu	2.476 /a/	3.098 /a/	0.653 /a/
Cr	2.725 /b/	4.382 /b/	
Fe	2.776 /a/	3.823 /b/	1.73 /b/
Ir	2.735 /a/	4.03 /a/	1.471 /a/
Ni	2.735 /a/	3.907 /a/	1.305 /a/
Pd	2.735 /a/	3.906 /a/	1.564 /a/
Pt	2.476 /a/	3.305 /b/	1.388 /a/
Rh	2.517 /b/	3.823 /b/	1.99 /a/
Zr			6.527 /b/

Table 3.1: Values of the chemisorption bond energies for H, O, CO on various metals. /a/ : Ref. 65, /b/ : Ref 23.

In table 3.1 we have collected from recent literatures /23,65/ values of the chemisorption energies of hydrogen, oxygen and carbon monoxide on metals. The segregation on clean and monolayer covered surfaces of metal alloys are calculated using eqs. (3.4) and (3.5). For this, data for the surface energies and heats of solution are taken from the work of Miedema et al. /67/. In table 3.2 heats of segregation for clean and covered surfaces are presented. It should be noted that the surface concentration can be easily calculated from heat of segregation (Q_{seg}) using eq. (3.1). As an example, results for surface concentration for clean and covered surfaces of Ni Cu alloy are shown in Fig 3.1.

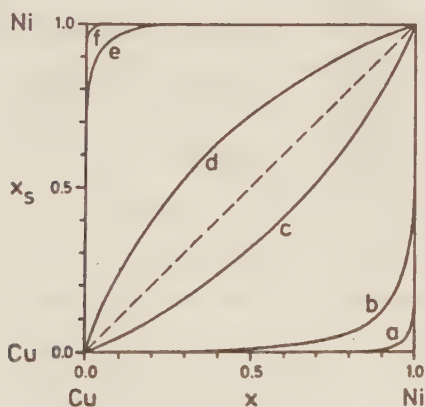


Fig. 3.1: Surface concentration x_s shown against bulk concentration x for Ni_xCu_{1-x} alloy. Curve a refers to a clean surface at $T=600K$. Curve b refers to a H-covered surface ($\theta=1$) at $T=300K$. Curves c and d refer to CO and O covered surface ($\theta=0.5$) at $T=600K$. Curves e and f refer to CO and O ($\theta=1$) at $T=600K$ respectively.

Alloy A-B	Segregating element (expt.)	Q_{Seg} (eV)	$Q_{\text{Seg}}^{\text{chem}}$ (H) (eV)	$Q_{\text{Seg}}^{\text{chem}}$ (O) (eV)	$Q_{\text{Seg}}^{\text{chem}}$ (CO) (eV)
Ag-Au	Ag	+0.1502			+0.0466
Ag-Cu	Ag	+0.402		+0.7749	+0.0394
Ag-Pd	Ag	+0.4911		+0.0599	-0.7832
Ag-Rh	Ag	+1.0671		+0.6112	-0.6423
Au-Cu	Au	+0.1233			-0.1357
Au-Ni	Au	+0.6693			
Au-Pd	Au	+0.3574			-0.8133
Cr-Pt	none	-0.1347	+0.114	+0.9428	
Cu-Ni	Cu	+0.3678	+0.1088	-0.461	-0.2849
Cu-Os	Cu	+1.21			
Cu-Ru	Cu	+0.88			
Fe-Cr	Cr	-0.0912	-0.0394	-0.6506	
Fe-Ni	Ni	-0.0663	-0.0247	-0.1699	+0.3585
Fe-Pt	none	-0.115	+0.1854	+0.403	+0.2269
Ni-Pd	Pd	-0.1741	-0.1741	-0.1741	-0.4331
Ni-Pt	none	+0.0083	+0.2673	+0.6299	-0.0746
Ni-Th	Th	-0.8982			
Pd-Pt	Pd	+0.287	+0.546	+0.8879	+0.4631
Pt-Au	Au	-0.5657			+0.4289
Pt-Cu	Cu	-0.5035	-0.5035	-0.2963	+0.2321
Pt-Ir	Pt	+0.3388	+0.0798	-0.3864	+0.2559
Pt-Os	Pt	+0.5729			
Pt-Rh	Pt	+0.1046	+0.0632	-0.4134	-0.5066
Sn-Au	Sn	+0.6299			
Sn-Cu	Sn	+0.9759			
Sn-Fe	Sn	+1.7643			
Sn-Pt	Sn	+1.3499			
Zr-Fe	Zr	+0.1917			+4.9883

Table 3.2: Heats of segregation of the solute A for clean and monolayer covered surfaces of dilute alloy A_xB_{1-x} . A positive (negative) value of Q_{seg} corresponds to segregation of solute (solvent); the magnitude of Q_{seg} is a measure of segregation strength. Experimental values of column 2 are taken from Ref /46/ and references cited therein.

3.2. SEGREGATION IN SMALL CLUSTERS OF ALLOYS

Metal alloys have widespread application as catalyst in many chemical reactions. This is due to the fact that by alloying, a catalyst's activity for a number of reactions can be changed [3-5]. Depending on the alloy constituents, undesirable reactions are 'poisoned' while the desirable reactions are 'promoted', thereby enhancing the selectivity of the catalyst by significant amount. In industrial applications mostly catalysts are in the form of small clusters of the size varying from ~ 1 nm to 100 nm. Alloy clusters of this small size exhibit quite different mixing and segregation behaviour compared to that of larger clusters, mainly due to increased surface to volume ratio. For example, it has been observed Cu-Ru and Cu-Os alloys exhibit no miscibility in the bulk [22], whereas in the form of very small clusters they can be found in various composition range. The use of these bimetallic cluster catalysts in ethane hydrogenolysis and conversion of cyclohexane has proven to be a big landmark in heterogeneous catalysis [5]. As it is well known, the surface composition of alloy catalysts play the deciding role in its catalytic property, it is therefore worthwhile to investigate the effect of cluster size on surface segregation phenomena. In this section we will study the segregation behaviour of highly dispersed alloys and will investigate the case of Cu-Ru and Cu-Os alloys as examples.

In writing eq. (3.1) for surface composition of an alloy we didnot take the size of the sample into account. In the case of finite-sized samples, the surface and bulk concentrations are related and can be obtained by a simple relation,

$$x_B N_B + x_S N_S = x_{av} N_T \quad (3.6)$$

Here, N_T is the total number of atoms in the particle and N_B and N_S are the number of atoms in the bulk and on the surface. x_{av} is the average concentration. Combining eqs. (3.1) and (3.5) we obtain,

$$\frac{x_S}{1 - x_S} = \frac{x_{av} - D x_S}{(1 - x_{av}) - D(1 - x_S)} \exp(Q_{seg}/kT) \quad (3.7)$$

where D is the dispersion of the particle, given by $D = N_S / N_T$. The important limits of the eq. (3.7) have been discussed by Helms /21/, and here we will point them out. If $x_{av}/D \gg 1$, the particle size effect is negligible; for $x_{av}/D \sim 1$ (even for small D) particle size effects are important. If $\exp(Q_{seg}/kT) \gg 1$, then $x_S = x_{av}/D$ or 1, whichever is smaller.

We apply eq. (3.7) to calculate segregation in small clusters of Cu-Ru and Cu-Os alloys. As mentioned earlier, these alloys show almost no miscibility in the bulk (i.e. strong segregation of one component) but in form of small clusters with $D = 0.5 - 1$ they are available in different concentration range. In order to take cluster effects in the heat of segregation, we have to modify eq. (3.4). In eq. (3.4) the factor $1/3$ appears due to the fact that on the average one-third of the bulk bonds are broken at the surface of polycrystalline sample - a fact not necessarily true for small cluster surfaces. In general, the fraction of broken bulk bonds ($\bar{f}$) for small cluster surfaces depend upon geometrical shape and dispersion of the cluster. We calculate this factor $\bar{f}$, for two well known geometries namely - icosahedra and cubooctahedra (Fig. 3.2). It is theoretically and experimentally /68/ established that the small metal clusters

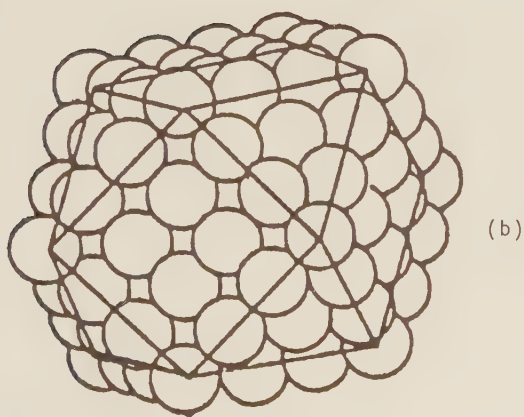
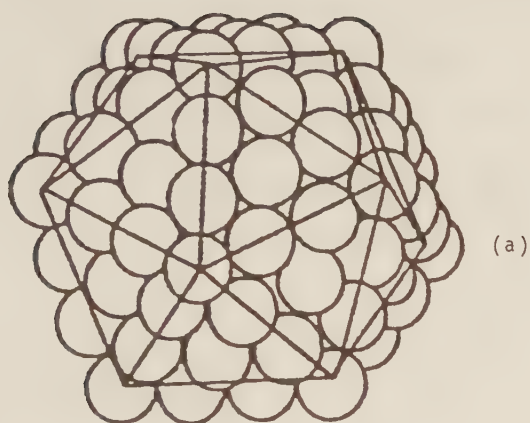


Fig 3.2: Icosahedral (a) and cubooctahedral (b) clusters with 147 atoms.

are found in close-packed structures similar to icosahedral and cubooctahedral shape, icosahedra being more stable for very small clusters. Unlike the clean surface of a semi-infinite sample, the number of missing bonds of the surface atoms for icosahedra- and cubooctahedra- shaped clusters vary from site to site. But for simplicity we assume all sites on the surface of icosahedra and cubooctahedra clusters to be equivalent and calculate the average number of broken bonds per surface atoms. These values are given in table 3.3.

N_T	N_S	D	Fraction of bulk bonds broken at the surface for :	
			Icosahedra ($\bar{f}_I$)	Cubooctahedra ($\bar{f}_C$)
13	12	0.92	0.5	0.583
55	42	0.76	0.381	0.452
147	92	0.63	0.337	0.402
309	162	0.52	0.315	0.377
561	252	0.45	0.302	0.361
923	362	0.39	0.293	0.351
1415	492	0.35	0.287	0.343
2057	642	0.31	0.282	0.338

Table 3.3: Fraction of broken bonds at the surface of an icosahedral and cubooctahedral cluster with dispersion D. N_T and N_S are the total number of atoms in cluster and number of atoms on the surface respectively.

The heat of segregation of alloy cluster is given as, from eq. (3.4)

$$Q_{seg} = \bar{f} \cdot \bar{Q} \quad (3.8)$$

where $\bar{f}$ is $\bar{f}_c$ ($\bar{f}_I$) for cubooctahedra (icosahedra) cluster and $\bar{Q}$ is given by,

$$\bar{Q} = \left[f \Delta H_{sol}(A,B) - g(\gamma_A - \gamma_B)\sigma_A \right] \quad (3.9)$$

The quantities in right hand side of eq. (3.9) have same meaning as in eq. (3.4).

Now, using heat of solution and surface energy data of Miedema /67/, we calculate Q for Cu-Ru and Cu-Os alloys and obtain $Q(\text{Cu-Ru}) = 254.8 \text{ kJ/mol}$ and $Q(\text{Cu-Os}) = 350.41 \text{ kJ/mol}$. From this we obtain for polycrystalline surface, taking $\bar{f} = 1/3$, heats of segregation for a semi-infinite sample of Cu-Ru and Cu-Os alloys to be 84.933 kJ/mol and 116.803 kJ/mol respectively. These large values of Q_{seg} indicate very strong segregation of Cu at the surface of these alloys, which is in accordance with the experimental fact that these alloys exhibit almost no miscibility. Using eqs. (3.8) and (3.7) we calculate the surface concentration X_s for icosahedral and cubooctahedral samples of Cu-Ru and Cu-Os alloys with $X_{av}(\text{Cu}) = 0.01$ (see fig.3.2).

The values of X_s for Cu-Ru and Cu-Os alloys fall on the same curve for icosahedral and cubooctahedral samples, which indicate that the geometrical shape of alloy sample doesnot play any role in their segregation behaviour. However, we obtain rather small segregation of

Cu in highly dispersed samples ($D \sim 0.5 - 1$). This result conforms with the experimental fact that small clusters of Cu-Ru and Cu-Os exhibit miscibility unlike in the large aggregates and can have compositions far outside the range of those possible in a bulk solid solution of the metal components.

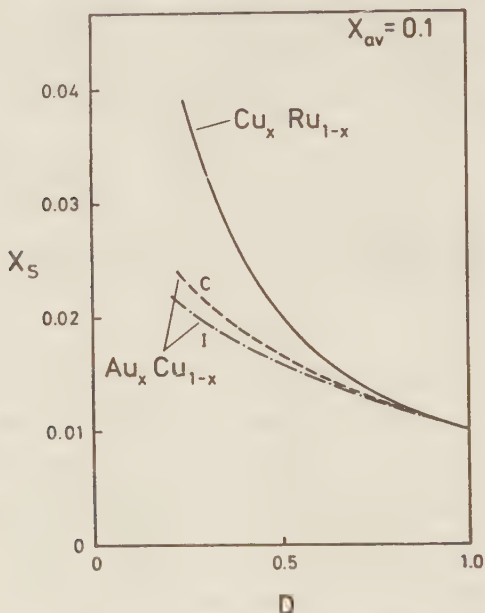


Fig. 3.2: Surface concentration x_s , with $x_{av} = 0.01$ and $T = 1000K$ shown against dispersion. Full curve corresponds to Cu-Ru alloy, with results for icosahedra and cubooctahedra clusters falling on the same line. Dashed and dot-dashed curves refer to cubooctahedral and icosahedral samples of Au-Cu alloy respectively.

Due to very large value of Q_{seg} for Cu-Ru and Cu-Os alloys, we are in the limit $\exp(Q_{seg}/kT) \gg 1$, and therefore from eq. (3.7) $X_s \sim X_{av}/D$ or $1 -$ which suggests that the segregation in icosahedral and cubooctahedral samples are same. But for alloys with smaller Q_{seg} this shape effect may be important and to test that we have shown in

fig. 3.2 results for Au-Cu alloy ($Q_{seg} = 11.9$ kJ/mol). Curves C and I refer to cubooctahedral and icosahedral samples respectively, and one obtains slightly larger segregation in more opened cubooctahedral sample than in icosahedral sample.

3.3 ABSORPTION INDUCED SEGREGATION IN ALLOY : H/Pd_xZr_{1-x}

Recently, it has been experimentally observed that the absorption in bulk of glassy metal alloy Pd-Zr has a strong effect on the surface segregation property of that alloy [70]. Experiment was performed on the Pd_{0.35}Zr_{0.65} glassy sample which under normal conditions does not exhibit any surface segregation. However, upon hydrogen absorption, surface of the sample was found to be enriched in Pd with Pd-concentration $\sim 0.8 - 0.9$. As the heat of solution of hydrogen in Pd is -0.5 kJ/mol whereas of hydrogen in Zr is -76 kJ/mol [71], one might expect intuitively, that the observed surface segregation of Pd results from the large difference in the heat of solution of hydrogen in the individual constituents of the alloy. In the following, we will present a bond model for calculating surface segregation of Pd in Pd_xZr_{1-x} alloy. This theory can be easily applied to study similar effects in other systems.

In order to determine the hydrogen-induced surface enrichment of Pd in Pd_xZr_{1-x} alloy, we use a bond model for the interaction energies between Zr and Pd atoms in presence and in absence of hydrogen. In a non-dilute regular solution alloy, the heat of segregation Q_{seg} can be expressed in terms of the pair-bond energies, which for the surface can be written in terms of bond energies as [39],

$$Q_{seg} = \frac{Z_v}{2} \cdot (\epsilon_{Pd} - \epsilon_{Zr}) - 2 \omega Z_v \left(x - \frac{1}{2}\right) + 2 \omega Z_s (x_s - x) \quad (3.10)$$

The first term in the right-hand side represents the difference in the pair bond energies of Zr and Pd atoms. Z_l and Z_v are the coordination numbers within a plane and between two neighboring planes. Thus for a (100)-plane of fcc, $Z_l = Z_v = 4$, and the bulk coordination is $Z = Z_l + 2 Z_v$. ω is the alloy parameter, which is written in terms of Zr and Pd pair bond energies as,

$$\omega = \epsilon_{Pd,Zr} - \frac{1}{2} (\epsilon_{Pd} + \epsilon_{Zr}) \quad (3.11)$$

is related to the heat of mixing ΔH_m as,

$$\omega = \Delta H_m / Z \cdot x(1-x)$$

In the bond picture, the pair bond energy of a metal is related to its heat of vaporization as /69/,

$$\epsilon_i = -2 \frac{\Delta H_{vap}(i)}{Z}$$

Using this identity, the first term in eq. (3.10) is written as,

$$\frac{Z_v}{2} (\epsilon_{Pd} - \epsilon_{Zr}) = \frac{Z_v}{2} \Delta H_{vap}(Pd) \left[\left(\frac{\gamma_{Zr} \sigma_{Zr}}{\gamma_{Pd} \sigma_{Pd}} \right) - 1 \right] \quad (3.12)$$

where we have used the identity, $\Delta H_{vap} = K(\gamma \cdot \sigma)$, defined earlier; γ and σ being the surface tension and the molar surface area respectively. Note, eq. (3.10) is a non-dilute limit of eq. (3.4) with first term in eq. (3.10) being expressed as the difference in surface energies in eq. (3.4). Using Miedema's data /67/ for γ and the molar surface area σ , and experimental value for $\Delta H_{vap}(Pd)$

/72/, the difference of surface energies is 16.6 kJ/mol. From experimental data for the heat of mixing /73/ of $\text{Pd}_{0.35}\text{Zr}_{0.65}$ alloy, we get $\omega = -21 \pm 9$ kJ/mol. Solving eqs. (3.1) and (3.10) self-consistently, the equilibrium surface composition is calculated to be $\text{Pd}_{0.3}\text{Zr}_{0.7}$. Therefore, no observable surface segregation will occur at the experimental temperature $T = 423$ K. This result does not change even if we take large error in ω into account, and take $\omega = -10$ kJ/mol. Thus in absence of hydrogen we do not expect any segregation in $\text{Pd}_{0.35}\text{Zr}_{0.65}$, which seems in accordance with experiment.

In the case of hydrogen absorption in the bulk of Pd-Zr alloy, we take into account two important effects. Due to presence of hydrogen in the interstitial site, the alloy parameter ω must be modified (ω^H) and we include a correction term ($\Delta H'$) to the surface energies due to the absorbed hydrogen. Then, the heat of segregation is modified as,

$$Q_{\text{seg}} = \frac{Z_v}{2} (\epsilon_{\text{Pd}} - \epsilon_{\text{Zr}}) - 2 \omega^H Z_v (x - \frac{1}{2}) + 2 \omega^H Z_s (x_s - x) + \Delta H' \quad (3.13)$$

$\Delta H'$ involves essentially the different binding of absorbed H to the bulk Pd and Zr atoms and is given by,

$$\Delta H' = \Delta E_s(\text{Zr}) - \Delta E_s(\text{Pd}) \quad (3.14)$$

where $\Delta E_s(\text{Zr})$ and $\Delta E_s(\text{Pd})$ are the additional surface energy for Zr and Pd atoms respectively, resulting due to the presence of hydrogen. We determine ΔE_s as follows. We study a (100)-surface of fcc lattice where hydrogen is in octahedral interstitial positions. We now

consider the solution of H in pure Zr. The binding energy of a hydrogen atom in ZrH_y is, apart from an additive constant, the heat of mixing of Zr and metallic hydrogen per hydrogen atom. For low hydrogen concentrations, this is the heat of solution $\Delta H_{sol}(H, Zr)$ for H in Zr. Thus upon hydrogen absorption, the total cohesive energy of Zr will increase. The additional binding energy of a bulk Zr atom due to absorbed H is,

$$\Delta E_{Zr, H}^b = y \Delta H_{sol}(H, Zr) \quad (3.15)$$

Furthermore, we assume that this relation will hold also for the additional binding of Zr due to H in the alloy $Pd_x Zr_{1-x}$. Assuming a random distribution of H, $\Delta E_{Zr, H}$ will linearly depend on the number of nearest neighbor octahedral sites available for hydrogen. In the bulk of an fcc lattice, there are 6 such sites around an atom, whereas on the (100)-surface there is only one. Therefore, the additional binding energy of a surface Zr atom due to H will be,

$$\Delta E_{Zr, H}^b = \frac{1}{6} \cdot y \Delta H_{sol}(H, Zr) \quad (3.16)$$

Consequently, the additional surface energy due to bulk hydrogen absorption will be,

$$\begin{aligned} \Delta E_s &= \Delta E_{Zr, H}^s - \Delta E_{Zr, H}^s \\ &= -\frac{5}{6} y \Delta H_{sol}(H, Zr) \end{aligned} \quad (3.17)$$

Thus, the correction term to the surface energy γ^H is given as,

$$\Delta H' = -\frac{5}{6} \gamma \left[\Delta H_{sol}(H, Zr) - \Delta H_{sol}(H, Pd) \right] \quad (3.18)$$

Because of the large difference in the heats of solution of hydrogen in the alloy components, $\Delta H'$ is positive and will induce surface segregation of Pd even for low concentration of absorbed hydrogen.

As pointed out earlier /74/, the absorbed hydrogen will decrease the effective contact between bulk metal atoms, thereby decreasing the magnitude of the alloy parameter ω . However, it is difficult to obtain reliable value of ω^H and therefore in our numerical calculation we take ω^H as an input parameter. In order to obtain a reliable estimate for ω^H , following remarks are made. First, we expect that ω^H should be smaller in glassy alloys than in corresponding crystalline systems. Furthermore, as discussed previously /74/, ω^H will be only a fraction of the alloy parameter ω in the absence of hydrogen. This fraction should generally depend on the hydrogen concentration. In view of the results presented in Ref. 74, we expect ω^H to be of the order of 0.25 to 0.5 for hydrogen concentration between 20 - 50%.

Results for the equilibrium surface concentration x_s of Pd for different hydrogen concentration and for different values of the alloy parameter ω^H are presented in Fig. 3.2. From these results we see that for hydrogen concentration between 20 - 50%, one obtains for the surface concentration x_s of Pd, values between 0.6 and 0.9. This result compares well with the experimental result for $Pd_{0.35}Zr_{0.65}$

with absorbed hydrogen concentration ~ 0.2 .

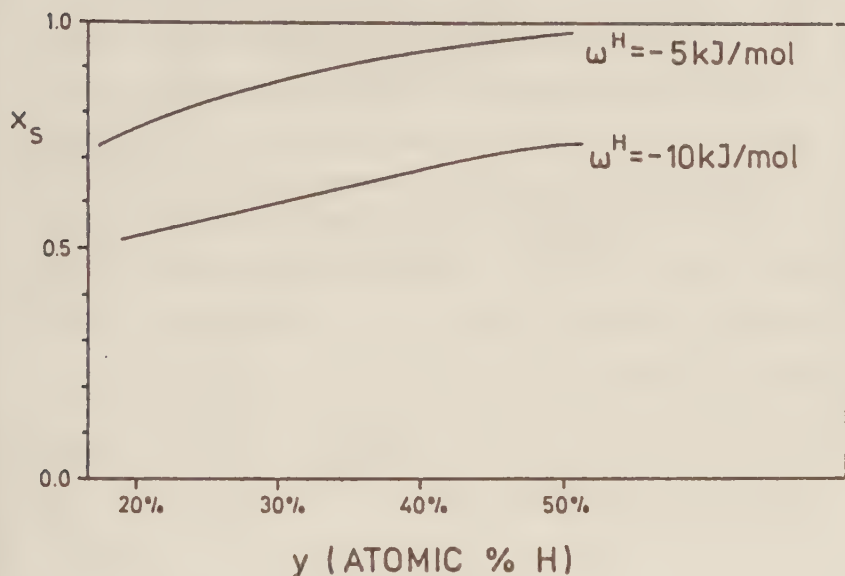


Fig. 3.3: Surface concentration x_s of Pd in $\text{Pd}_{0.35}\text{Zr}_{0.65}$ obtained from a self-consistent calculation using eqs. (3.1) and (3.13). The concentration of absorbed hydrogen is denoted by y . ω^H is taken to be a parameter.

3.4 DISCUSSION OF THE RESULTS

In this section we critically discuss the results obtained in earlier sections. Let us discuss first the eq. (3.4) describing the heat of segregation in dilute alloys. As it is well known, strain energy effects may influence surface segregation in alloys. Tsai et al. /75/ have pointed out that these effects are important if the solute is bigger in size than the solvent. In that case the solute will segregate to the surface. That this feature is also incorporated in eq. (3.4) can be shown as follows. Consider the term $(\gamma_A - \gamma_B)$,

which can also be written in terms of the heats of vaporization as,

$$\gamma_A \left[1 - \frac{V_A^{2/3} \Delta H_{vap}(B)}{V_B^{2/3} \Delta H_{vap}(A)} \right]$$

From this term it can be seen that the surface is enriched with the constituent having lower heat of vaporization or the bigger atomic size. As can be seen from comparison of the second and third columns of Table 3.2, we have calculated correctly which atoms are segregating to the surface. This overall agreement with experiment suggests that eqs. (3.1) and (3.4) should also give qualitatively the correct results for alloys whose constituents differ appreciably in size. Although for concentrated alloys, the validity of eqs. (3.4) and (3.5) are not clear, a qualitative change in surface segregation behavior is not expected.

For a surface covered with chemisorbed atoms, the heat of segregation is modified by a term describing the new surface bonds to the adsorbates. However, eq. (3.5) needs further modification in the case of island formation of the adsorbates. In that case, spatial fluctuation of the coverage occur which induce local variations of the surface segregation. With respect to the chemisorption induced surface segregation, note that the surface equilibrium concentration x_s , calculated from eqs. (3.5) and (3.1), will be achieved in the experiment after a time which depends on temperature and on the diffusion kinetics of the alloy. The observed concentration will change exponentially with time towards the equilibrium concentration. For Q_{seg} values very low in magnitude we expect no observable segregation. On the other hand, considerable segregation is expected to occur for high values of Q_{seg} even at relatively low temperatures.

This is confirmed by experiments. Thus, the chemisorption induced surface segregation should be observable at temperatures which are lower than the desorption temperature, but which are large enough so that surface segregation occurs within usual experimental observation times. This is not the case for chemisorbed hydrogen, which has a very low desorption temperature. As can be seen from the table 3.2, we do not expect a large change in the surface composition of an alloy upon hydrogen chemisorption. This is in agreement with experiments /76,77/. For oxygen and carbon monoxide chemisorption we expect a significant change in surface segregation. This is evident from tables 3.1 and 3.2, and fig. 3.1. The influence of CO and O chemisorption on surface segregation is illustrated by the curves c and d. Note the apparently large segregation corresponds to thermal equilibrium and can only be observed after a relatively long time.

Though only a few experimental situations are known on chemisorption induced segregation, our predictions agree with observations for O chemisorbed on Cu-Ni and Au-Ni and CO on Cu-Ni, Pt-Au, Ag-Pd, Au-Pd and Au-Ni alloy surfaces. In all these cases, one observes a reversal of the kind the atoms which segregate to the surface. From chemisorption data on chemisorption energies of O and CO (table 3.1), we note that both the magnitude and variation of chemisorption energy decreases as one goes from left to the right in the transition metal series. This variation is quite small in the noble metal end that is why we do not expect any significant change in the segregation behavior of noble metal - noble metal alloys. However, one will observe drastic effects for noble metal - transition metal alloys as discussed above. Furthermore, for transition metal alloys, whose constituents are not neighbors in the

periodic table, some significant changes can be expected as well. It can be seen from table 3.2 that for CO on Fe-Ni, Pt-Rh, Fe-Pt and O on Pt-Rh and Pt-Ir, we predict a reversal of the segregating element expected for clean surfaces. However, for CO on Fe-Zr and O on Fe-Cr and Ni-Pt, the clean surface segregation is enhanced. No experimental results are available on these systems. For Sn, no chemisorption energy data could be found. However, from the above discussions we expect significant changes in segregation in Sn alloys upon chemisorption. This is also supported by experimental data on CO covered Pt-Sn surfaces /76/.

Our calculated surface segregation behavior in alloys of small clusters, shown in Fig. 3.2, is interesting. It clearly predicts that the segregation tendency increases with cluster size. This effect is an artifact of the unsaturated dangling bonds on the surface of cluster atoms and due to the increased surface to volume ratio (dispersion) in case of small clusters. For clusters of Cu-Ru alloy we find a moderate segregation of Cu for clusters with dispersion about 50%, but with increasing cluster size Cu segregation increases abruptly. This is important in explaining the miscibility behavior of Cu-Ru samples as observed experimentally /7/. Clearly, in larger samples of Cu-Ru alloy, with small dispersion ($D < 0.1$), there will be a very strong segregation of Cu onto the surface - which makes this alloy not miscible in the bulk. However, in the form of small clusters, Cu and Ru can form stable alloy with moderate segregation of Cu at the surface. This unique feature is key to realisation of bimetallic cluster catalysts like Cu-Ru /5/. Same explanation will also hold for the segregation behavior of Cu-Os clusters which shows a very strong segregation of Cu at the surface. We also obtain that in

alloy clusters with moderate heat of segregation (e.g. Au-Cu), surface segregation also depends on cluster shape. The cubooctahedral shaped alloy clusters would show somewhat less segregation than icosahedral ones, which is caused due to more closed-packed nature of the latter cluster with relatively less unsaturated dangling bonds. It should be noted that the bond model, used here to calculate surface segregation in alloy clusters, has also been successfully applied to predict the stability of metal clusters [78-80].

It has already been mentioned in section 3.3 that, in case of absorbed hydrogen, a pair bond type model for hydrogen binding energy might only be of limited validity due to the long range interactions between H-atoms and the surrounding metal atoms. Therefore, we proceed more generally, using total energy arguments (involving the experimentally accessible heat of solution of hydrogen) rather than pair bond energies. Two effects are responsible for the surface segregation in $\text{Pd}_x\text{Zr}_{1-x}$ induced by bulk hydrogen absorption. First, due to hydrogen absorption, the surface energies of Pd and Zr will be changed considerably. Secondly, the alloy parameter ω , which suppresses the surface segregation in pure $\text{Pd}_x\text{Zr}_{1-x}$, decreases considerably due to H absorption. Note, the results presented in Fig. 3.3 depend sensitively on ω^H . Further studies to determine ω^H would be very valuable.

3.4.1 A general ternary interface problem:

The chemisorption and bulk-absorption induced surface segregation phenomena can be treated as special cases of the more general problems of segregation at interfaces or in ternary alloys. In the following

we briefly discuss the problem of the interface between an alloy $A_x B_{1-x}$ and a pure substance, shown in Fig. 3.4. The atomic

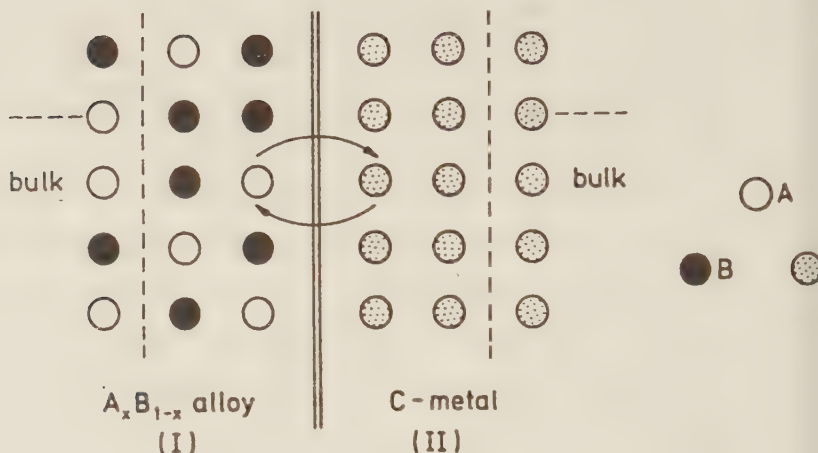


Fig.3.4: Illustration of segregation at the interface of an $A_x B_{1-x}$ alloy (I) and a metal C (II). Diffusion between I and II will occur, if the exchange of interlayer atoms (marked by arrows) is exothermic. After finite time only the atomic layers close to the interface will experience a change in composition.

segregation at the interface will be governed by the heats of exchange $Q_{ex}(A,C)$ and $Q_{ex}(B,C)$, describing the work involved in exchanging an A or B atom with a C atom across the interface. In the pair bond model we get,

$$Q_{ex}(A,C) = (1-x)(\epsilon_{AC} - \epsilon_{BC}) + (Z_l + 1) \left[(1+x)\omega_{AC} + (1-x)\omega_{BC} - (1-x)\omega_{AB} \right] \quad (3.19)$$

and

$$Q_{ex}(B,C) = x(\epsilon_{Bc} - \epsilon_{Ac}) + (Z_l + 1) \left[(2-x)\omega_{Bc} - x\omega_{AB} + x\omega_{Ac} \right] \quad (3.20)$$

If both $Q_{ex}(A,C)$ and $Q_{ex}(B,C)$ are positive, there will be no atomic diffusion across the interface. One expects only interface segregation in the $A_x B_{1-x}$ alloy, which depends on the metal C. This situation corresponds to the case of chemisorption induced segregation. Alternatively, for negative heats of exchanges, one expects exchange of atoms across the interface. Due to kinetic reasons, exchange of atoms will be confined in the layers close to the interface only. Consider a second possible case of a compound forming tendency between A and C much stronger than between A and B, or B and C. In this case, we expect a large interpenetration of A and C atoms, while the B atoms will be pushed out of the interface. In only a finite layer of C atoms is present on AB alloy, then it would be absorbed totally, pushing the B component to the surface. Such a case is very similar to the absorption induced segregation described earlier.

4. ELECTRONIC THEORY OF CHEMISORPTION AND ITS APPLICATION IN INTERPRETING COMPOUND FORMATION TENDENCIES AT TRANSITION METAL SURFACE : OXYGEN AND SULFUR ON Ni(100)

4.1 INTRODUCTION

In chapter 3, we have discussed the problem of interaction of gas atoms with metal alloy surfaces, leading to a possible change of surface composition of the alloy surface. We have also seen that for some alloys, gas absorption (in bulk) can also influence the surface segregation. In this chapter we shall look into the microscopic mechanism of the gas-surface interaction, and as an example we shall treat the problem of oxygen and sulfur chemisorption on nickel surface. The problem of oxygen interaction with nickel surface has drawn lot of attention in recent years from experimental /81-89/ as well as theoretical /90-101/ points of view. Oxygen is found to be adsorbed dissociatively on nickel surfaces /30-33/, with chemisorption binding energy being 4 - 5 eV /23/. The low energy electron diffraction (LEED) measurements /81/ show that at low coverages oxygen atoms form a $p(2 \times 2)$ structure (Fig. 4.1), which changes to a $c(2 \times 2)$ structure at a higher coverage. In both these structures oxygen atoms are centered in the four-fold hollow sites with their nuclei about $0.9 \text{ \AA}$ above the surface nickel layer /82,83/. This result has also been confirmed more recently using He-diffraction measurements /84/.

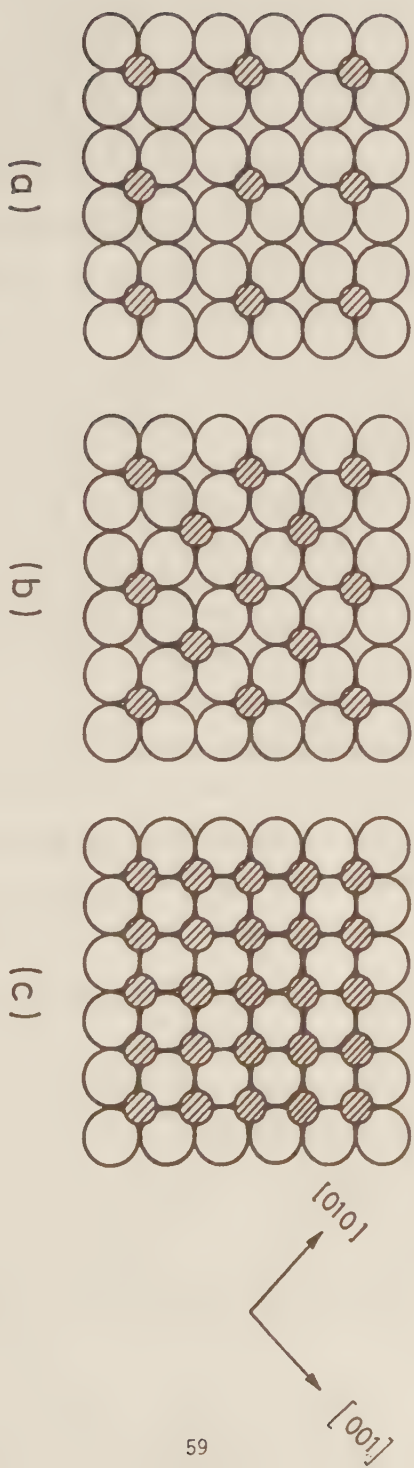


Fig. 4.1 : Illustration of Ni(100) geometry and oxygen overlayer structure for (a) $p(2 \times 2)$, (b) $c(2 \times 2)$ and (c) $p(1 \times 1)$ geometries. Nickel atoms are denoted by open circles and adatoms by crossed ones.

Ultraviolet photoemission (UPS) /85,86/ and ion neutralization (INS) /87/ spectroscopic measurements show an oxygen derived peak at about 5.5 eV below the Fermi energy (E_F). Recent inverse photoemission spectroscopic measurements /88,89/ indicate the existence of antibonding states about 0.5 - 1 eV above E_F , which grows with oxygen coverage.

Coverage dependent effects on the growth of the oxygen overlayer on nickel surface are also available /34-38/ and they can be summarized as follows. At low coverages, islands of $p(2 \times 2)$ structures are observed, which get saturated at quarter monolayer coverage. With increasing coverage, $c(2 \times 2)$ structure is observed to form and gets saturated at half monolayer coverage. Around or above half monolayer coverage oxidation of the surface nickel layer starts taking place, which prevents the observation of a $p(1 \times 1)$ structure. As initially a $p(2 \times 2)$ structure is favored over a $c(2 \times 2)$ structure, one can infer that the binding energy of the oxygen atoms should be larger in the $p(2 \times 2)$ structure than in the $c(2 \times 2)$ one. Although, a $p(1 \times 1)$ structure is never observed, it is likely that locally a $p(1 \times 1)$ structure is formed which acts as a nucleation centre for the surface oxidation.

There have been a number of theoretical studies of oxygen chemisorption on nickel (100) surface, but a complete understanding of the coverage dependent changes in the binding energy is not available. Liebsch /90/ performed a non-self-consistent Korringa-Kohn-Rostoker (KKR) calculation with muffin-tin potential, Wang and Freeman /91/ performed a self-consistent LCAO calculation and Bullett and Cohen /92/ used localised orbital method for studying O/Ni(100) system. All these calculations were able to reproduce the large adsorbate-induced

"bonding" peak below the d-band and the small "antibonding" peak just above E_F . Desjonquieres and Cyrot-Lackmann /93/ presented a tight-binding calculation taking only nickel 3d-band and oxygen 2p-orbitals. Recent calculations by Godby et al. /94/ discuss the importance of the hybridization between nickel 4s4p and oxygen 2p orbitals in the electronic structure of the system. The importance of hybridization between O 2p and Ni 4s orbitals was also pointed by Walch and Goddard /95/ in their generalised valence bond calculation. Chakraborty et al. /96/ used an effective medium approach /102/ to investigate the chemisorption and incorporation process of oxygen on nickel surfaces. But despite all these calculations on this system, the role of coverage dependent changes in binding energy and electronic structure of O/Ni system has not been studied so far.

Unlike the O/Ni(100) system, not many literature exist on sulfur absorption on nickel. LEED measurements /103/ by Van Hove and Tong indicate that sulfur also forms four-fold coordinated $p(2 \times 2)$ and $c(2 \times 2)$ structures on Ni(100) with their nuclei about 1.3 Å above the surface nickel plane. This data is also in accordance with recent electron energy loss spectroscopic measurements /104/. Angle resolved photoemission spectroscopic measurements /105/ on S/Ni(100) indicate the occurrence of sulfur derived peaks at about 4.5 - 5 eV below E_F which are about 1 - 2 eV wide. There does not exist detail investigation of coverage dependent changes of the growth of sulfur layer. Theoretical investigations on S/Ni(100) system is also limited. However, earlier cluster calculations /106/ suggest that, like in oxygen, sulfur adsorption on nickel takes place through a strong hybridization of S 3p and Ni 4s4p orbitals.

In the light of above experimental and theoretical results, it is worthwhile to reexamine the binding and the details of the electronic structure and their coverage dependence for oxygen and sulfur chemisorption on Ni(100). In the following, we will present a detail tight-binding calculation of the chemisorption binding energy and the local electronic density-of-states for oxygen and sulfur chemisorption on nickel (100) at various coverages. The electronic structure is determined by taking explicitly 3d and 4s electrons and their hybridization for substrate nickel, and 2p and 3p orbitals for oxygen and sulfur respectively. The binding energy per adsorbate atom is calculated as a function of adsorbate coverage. These results will be discussed in connection with the compound formation tendencies at higher coverages, with a particular emphasis given on oxidation of nickel. In section 4.2 we present the model and the method of calculation. Results for the clean Ni(100), O/Ni(100) and S/Ni(100) will be presented in subsequent sections.

4.2 THEORY OF CHEMISORPTION ON TRANSITION-METALS

The valence electron structure of transition-metals consists of tightly bound d-bands which hybridize with nearly free-electron sp bands. Most of the physical and chemical properties of the transition-metals are primarily governed by their d-electrons /107/. However, the sp-electrons play an important role in the chemisorption process. This happens due to the fact that the electrons of the adsorbate atoms first interact with the free-electron like charge cloud near the metal surface and form a chemical bond. Recent effective medium calculations /102/ have established this viewpoint and conclude that for a given adsorbate atom the contribution to

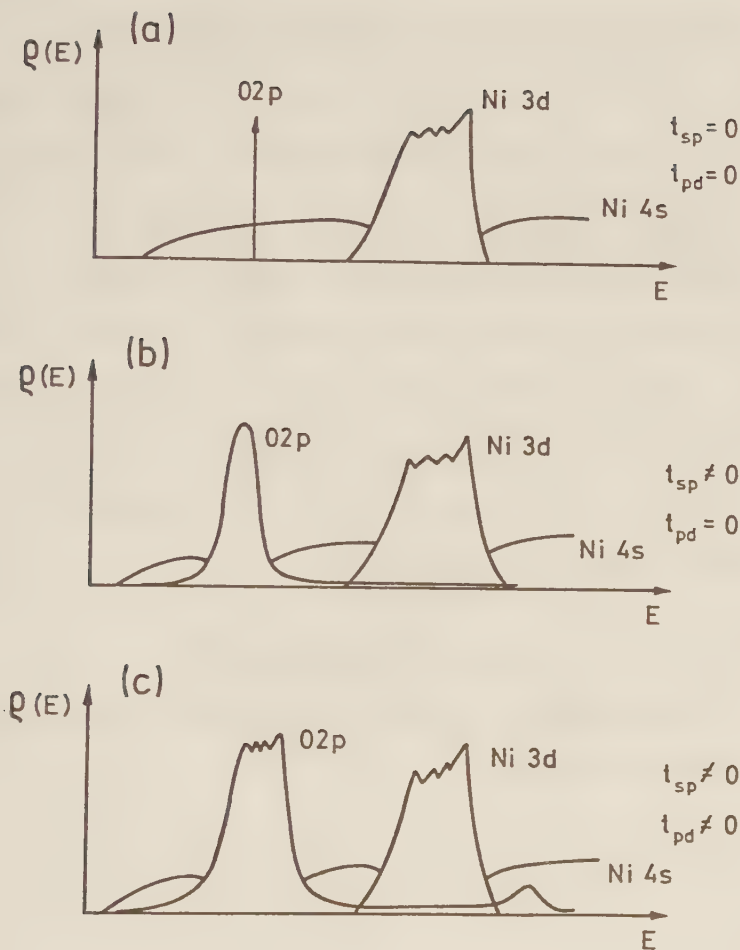


Fig. 4.2 : Schematic illustration of the role of hybridization between oxygen and nickel on their electronic density-of-states. (a) Without any hybridization, O 2p-states are atomic-like, (b) hybridization of O 2p-states with Ni 4s band produces a resonance about 0.5 eV wide and 5.5 eV below the Fermi level, (c) hybridization with Ni 3d band partially expels antibonding tail of the resonance giving a small peak above the d band.

chemisorption binding energy due to the homogeneous free electron gas is nearly same for all elements in the transition-metal series /108/. The d-electrons also add a contribution to this chemisorption binding energy which vary from element to element. For chalcogenide (like oxygen or sulfur) chemisorption on transition metal surfaces, essential facts about the electronic structure can be understood from the abovementioned arguments. First, the atomic p-orbital of the adsorbate atom hybridizes with metal sp-electrons, its centre-of-gravity is shifted thereby and the level is broadened. When this broad level hybridizes with the d-band of the metal, it gets broadened further and an antibonding peak appears just above the metal d-band. This is schematically presented in Fig. 4.2. We will see in the subsequent sections that a similar kind of picture acutally emerges from a realistic calculation.

4.2.1 Hamiltonian of the substrate adsorbate system

The tight-binding s-d Hamiltonian describing the transition-metal substrate is written as,

$$H^0 = H_s + H_d + H_{s-d} \quad (4.1)$$

where,

$$H_s = \sum_i |i,s\rangle \epsilon_{i,s} \langle i,s| + \sum_{i,j, i \neq j} |i,s\rangle t_{ij}^{ss} \langle j,s| \quad (4.2)$$

$$H_d = \sum_{i,\alpha} |i,\alpha\rangle \epsilon_{i,\alpha} \langle i,\alpha| + \sum_{i,j, \alpha\beta, i \neq j} |i,\alpha\rangle t_{ij}^{\alpha\beta} \langle j,\beta| \quad (4.3)$$

$$H_{s-d} = \sum_{i,j, \alpha, i \neq j} |i,s\rangle t_{ij}^{s\alpha} \langle j,\alpha| \quad (4.4)$$

Here $\epsilon_{i,s}$ is the centre-of-gravity of the s-band, $\epsilon_{i,\alpha}$ is the centre-of-gravity of the d-band with orbital type α ($\alpha \equiv d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{3z^2-r^2}$). $t_{ij}^{\alpha/\beta}$ is the electron hopping integral between orbitals α and β located at sites i and j respectively.

The Hamiltonian describing the adsorbate electrons (say, p-electrons) and their interaction with substrate valence electrons is,

$$H_a = H_a^0 + H' \quad (4.5)$$

where,

$$H_a^0 = \sum_{i,\alpha} |i,\alpha\rangle \epsilon_{i,\alpha}^a \langle i,\alpha| \quad (4.6)$$

$$H' = \sum_{\substack{ij,\alpha\beta \\ i \neq j}} |i,\alpha\rangle t_{ij}^{pd} \langle j,\beta| + \sum_{\substack{ij,\alpha \\ i \neq j}} |i,\alpha\rangle t_{ij}^{sp} \langle j,s| \quad (4.7)$$

$$\alpha \equiv p_x, p_y, p_z ; \beta \equiv d_{xy}, \dots, d_{3z^2-r^2}$$

Therefore, the total hamiltonian matrix of the substrate-adsorbate system has the following form,

$$[H] = \begin{bmatrix} H^0_{(6 \times 6)} & H' \\ H' & H_a^0_{(3 \times 3)} \end{bmatrix} \quad (4.8)$$

Our main aim would be to calculate first the local electronic density-of-states (LDOS) of the system (on adsorbate and substrate atoms), which for an orbital α at site i is written as,

$$\rho_{i,\alpha}(E) = -\pi^{-1} \text{Im} \langle i, \alpha | [E - H]^{-1} | i, \alpha \rangle \quad (4.9)$$

where,

$$\langle i, \alpha | [E - H]^{-1} | i, \alpha \rangle = \left[E - a_{i\alpha} - \frac{b_{1\alpha}^2}{E - a_{2\alpha} - \frac{b_{2\alpha}^2}{\ddots}} \right]^{-1} \quad (4.10)$$

Here, $a_{i\alpha}$ and $b_{i\alpha}$ are the continued fraction coefficients, which are determined using the recursion method /109,110/ (see Appendix B).

4.2.2 Expression for chemisorption binding energy

The chemisorption binding energy ΔE_B per adatom can be expressed in terms of the change in the local density-of-states of the tight-binding orbitals of the adatoms and of the transition-metal atoms, upon adsorption. Therefore, if $\rho_{i\alpha}(E)$ and $\tilde{\rho}_{i\alpha}(E)$ denote the local density-of-states for an orbital α at site i , before and after chemisorption respectively, the binding energy can be written as,

$$\Delta E_B = \sum_{i,\alpha} \left[\int_{-\infty}^{E_F} (\tilde{\rho}_{i,\alpha} - \rho_{i,\alpha}) E \, dE \right] - \Delta E_{\text{corr}} \quad (4.11)$$

where ΔE_{corr} is the change in the Hartree and exchange-correlation energies due to chemisorption which are counted twice in the first

term of eq. (4.11), and it can be expressed as,

$$\Delta E_{\text{corr}} = \frac{1}{2} (\Delta E_{\text{Coul}} + \Delta E_{\text{xc}}) \quad (4.12)$$

where,

$$\Delta E_{\text{Coul}} = \Delta \sum_{\substack{i \neq j \\ \alpha, \beta}} \iint d^3 \underline{r} d^3 \underline{r}' \frac{n_{i\alpha}(\underline{r}) n_{j\beta}(\underline{r}')}{|\underline{r} - \underline{r}'|} \quad (4.13)$$

In local density approximation,

$$\Delta E_{\text{xc}} = \Delta \sum_{i\alpha} \int d^3 \underline{r} \varepsilon_{\text{xc}}[n_{i\alpha}(\underline{r})] n_{i\alpha}(\underline{r}) \quad (4.14)$$

Here $n_{i\alpha}(\underline{r})$ is the charge density associated with the orbital (i, α) before adsorption, $\varepsilon_{\text{xc}}[n_{i\alpha}(\underline{r})]$ is the exchange-correlation energy density and the changes refer to that between after and before chemisorption. If the exchange-correlation potential and ε_{xc} is treated in $n^{1/3}$ /111/ approximation, then the correction term can be written as (see Appendix C for the derivation),

$$\Delta E_{\text{corr}} = \frac{1}{2} \sum_{i,\alpha} \Delta \epsilon_{i\alpha} (\tilde{N}_{i\alpha} + N_{i\alpha}) \quad (4.15)$$

where,

$$N_{i\alpha} = \int_{-\infty}^{E_F} \rho_{i\alpha}(E) dE \quad ; \quad \tilde{N}_{i\alpha} = \int_{-\infty}^{E_F} \tilde{\rho}_{i\alpha}(E) dE \quad (4.16)$$

and

$$\Delta \epsilon_{i\alpha} = \tilde{\epsilon}_{i\alpha} - \epsilon_{i\alpha} = \int_{-\infty}^{+\infty} E (\tilde{\rho}_{i\alpha} - \rho_{i\alpha}) dE \quad (4.17)$$

Here $N_{i\alpha}$ ($\tilde{N}_{i\alpha}$) is the charge (electron occupation number) associated with orbital (i, α) before (after) chemisorption and $\Delta\epsilon_{i\alpha}$ is the change in the mean energy of the orbital due to chemisorption. Therefore, eq. (4.11) can be rewritten as,

$$\Delta E_B = \sum_{i\alpha} \left[\int_{-\infty}^{E_F} (\tilde{\rho}_{i\alpha} - \rho_{i\alpha}) E dE - \frac{1}{2} \Delta\epsilon_{i\alpha} (\tilde{N}_{i\alpha} + N_{i\alpha}) \right] \quad (4.18)$$

In eq. (4.18) the summation over i runs through all atoms, including the adatom, which participate in chemisorption, and the summation over α runs through the corresponding orbitals. As chemisorption is a local phenomena (i.e. the LDOS of the adatom and its neighboring substrate atoms are changed), the summation in eq. (4.18) is taken over a cluster of a few atoms. For a four-fold chemisorption site on a (100) face of a fcc lattice we take a cluster of five atoms (Fig. 4.3).

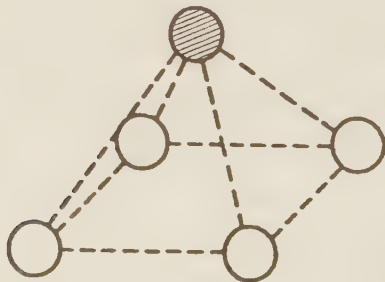


Fig. 4.3: Local chemisorption geometry on (100) surface of fcc lattice. The adsorbate atom is marked by crossed circle.

4.3 METHOD OF CALCULATION AND CHOICE OF PARAMETERS

The calculation of the electronic structure of oxygen and sulfur chemisorbed on nickel surface involves a few steps. At first we calculate the LDOS of bulk nickel using the recursion method described in Appendix B. The valence electrons (4s and 3d) of nickel are described by the tight-binding Hamiltonian (Eq. 4.1). The hopping integrals between orbitals on neighboring and next-neighboring atoms are obtained from the Slater-Koster /112/ parameters $dd\sigma$, $dd\pi$, $dd\delta$, $sd\sigma$ and $ss\sigma$. These parameters were taken from the band structure calculation of Dempsey et al. /113/ and given in Table 4.2. Using these parameters the Hamiltonian matrix was set up and tridiagonalised to obtain the continued fraction coefficients. We have used a fcc cluster of

Parameter	Value (eV)	
	nn	nnn
$dd\sigma$	-0.46137	-0.04068
$dd\pi$	0.25878	0.00653
$dd\delta$	-0.04381	0.00109
$sd\sigma$	-0.63036	-0.15048
$ss\sigma$	-1.80603	-0.36994

Table 4.2: Slater-Koster parameters for nickel with nearest neighbor (nn) and next nearest neighbor (nnn) interactions. From ref. /113/.

6084 atoms for describing the nickel lattice and obtained the continued fraction coefficients upto 20 levels. The LDOS was

calculated from the continued fraction coefficients using Beer-Pettifor truncation scheme /114/ (see Appendix B). The mean energies of the d and the s bands were chosen to be -1.345 eV and 1.303 eV, so that the Fermi level is at zero energy and the total occupation of the band ($N_s + N_d$) is 10. Integrating over the LDOS we found the bulk electronic configuration of Ni to be $4s^{0.606} 3d^{9.394}$.

Next, we calculate the LDOS on an atom situated on the (100)-surface of the lattice. We have used the bulk hopping integrals for the surface atoms. The mean energies (centres of gravity) of the 4s and 3d bands at the surface were adjusted and shifted rigidly with respect to their corresponding bulk values to obtain the same charge configuration as in the bulk. $\Delta\epsilon_{d,s}$ obtained in this way were kept fixed for all further calculations.

After completing these calculations, we place the oxygen adatoms onto (100) surface nickel plane forming a p(2x2), c(2x2) or a p(1x1) (see Fig. 4.1), and their nuclei at $0.9 \text{ \AA}$ above the surface Ni-atom nuclei. The adatom oxygen is described by its 2p-electrons and were allowed to hybridize with the nickel 4s and 3d orbitals. The corresponding set of hopping integrals were obtained from the parameters $pd\sigma$, $pd\pi$ and $sp\sigma$, given in Table 4.3. The parameters $pd\sigma$ and $pd\pi$ were taken from the calculations by Matheiss for NiO compound /115/ and hence were scaled properly for the oxygen-nickel distance of $1.98 \text{ \AA}$ (oxygen-nickel distance in NiO compound is $2.08 \text{ \AA}$). This scaling was done by assuming $1/r^5$ dependence for the hopping integrals /116/. The oxygen 2p-orbital energy was chosen as the mean of its ionization (-13.62 eV) and electron affinity (-1.47 eV) energies /117/ and scaled such that the vacuum level lies at 4.5 eV

(work function of Ni) above E_F . In this way we found the oxygen 2p-orbital to lie 3 eV below E_F . After setting up the hamiltonian for the adsorbate-substrate system, the LDOS for oxygen orbitals and its nearest neighbor nickel orbitals were calculated. The mean energies of surface Ni 4s and 3d bands were adjusted such that the total charge, on oxygen plus its neighboring nickel atoms, is same after and before chemisorption. Note, in this way we took care of the charge transfers between oxygen and its neighboring nickel atoms for all three overlayer structures in a consistent manner. This can be explained as follows. We have restricted the global charge neutrality condition to a cluster of 5 atoms, including oxygen and its four neighboring nickel atoms, shown in Fig. 4.3. As we assume the interaction between oxygen and its neighboring nickel atoms, all four surface nickel atoms will contribute equally to the transferred charge to oxygen. This will lead to the situation that in $p(2 \times 2)$ structure quarter of the net transferred

Parameter	Value (eV)	
	Oxygen	Sulfur
$pd\sigma$	-1.03676	-1.72794
$pd\pi$	0.47485	0.91499
$sp\sigma$	2.5	2.5

Table 4.3: Slater-Koster parameters for the neighboring interaction between nickel and oxygen and nickel and sulphur atoms. The first two values are from ref. /115/ (oxygen) and from ref. /118/ (sulfur). $sp\sigma$ was estimated from the values given in ref. /112/ for s-p metals.

charge to oxygen will come from each nickel atom. In $c(2 \times 2)$ structure each nickel atom will contribute half of the transferred charge, and in $p(1 \times 1)$ structure each nickel atom will contribute the net transferred charge to oxygen atom. We believe that this global charge neutrality criterion is essential for obtaining a meaningful charge transfer in chemisorption process and will show later that our calculated charge transfer values agree very well with other self-consistent ab-initio calculations.

For sulfur chemisorption on Ni(100) surface, we repeat the same steps as above. The hopping parameters for the interaction between sulfur 3p and nickel 4s and 3d electrons were taken from the work by Boudville et al. /118/ (Table 4.3) and scaled for the sulfur-nickel distance of $2.19 \text{ \AA}$. The sulfur 3p-orbital energy was set at 1.71 eV below E_F , which was obtained from its ionization (-10.36 eV) and affinity (-2.07 eV) energies /117/, as discussed above.

4.4 RESULTS AND DISCUSSIONS

4.4.1 Clean Ni(100) surface

In Fig. 4.4 we present our calculated LDOS spectra for bulk Ni and Ni(100) surface. The details of the spectra can be seen in Fig. 4.5 where we show the partial LDOS projected for each orbitals. From Fig. 4.4 we observe that the effective width of the Ni 3d-band is ~ 4 eV and its gets slightly narrower at the surface, which is evident due to unsaturated bonds. Furthermore, we see that LDOS at the Fermi energy is mostly of d-character. Also the degeneracy of the orbitals d_{xy} , d_{yz} and d_{xz} are lifted at the (100) surface, where only d_{xy} and d_{xz} remains degenerate. The orbitals d_{xy} , d_{xz} , $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ at

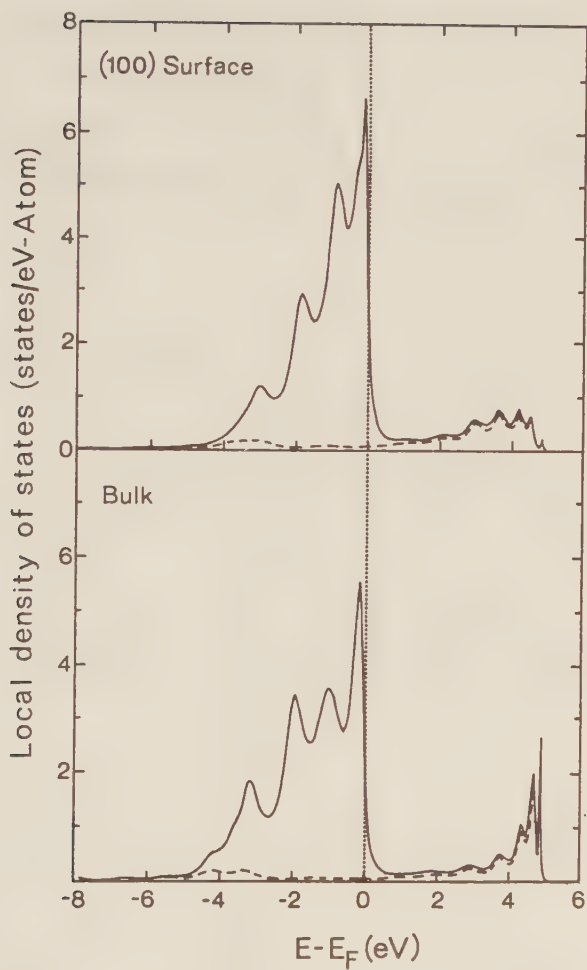


Fig. 4.4 : Local electronic density-of-states of nickel in bulk and on clean (100) surface. The dashed line refers to s-band contribution and the full line to s and d-band contributions.

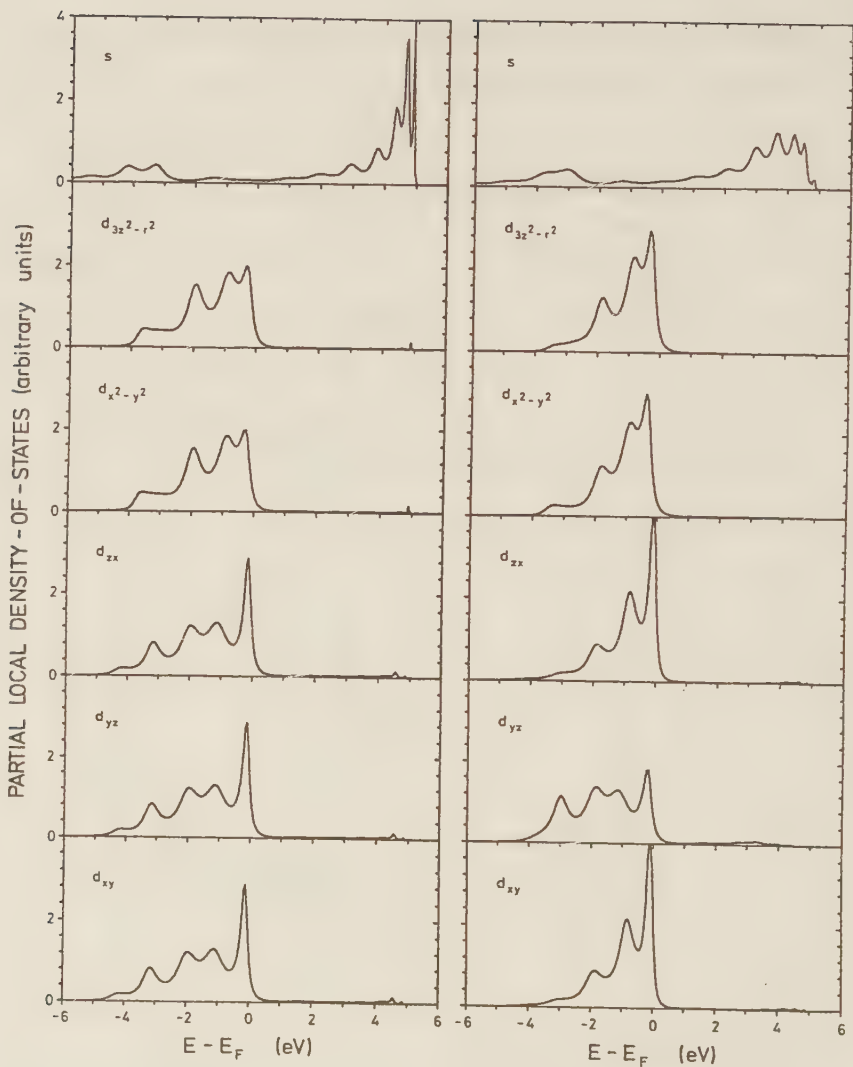


Fig. 4.5 : Partial local density-of-states projected for each orbitals of nickel, in bulk (left), and on clean (100) surface (right). The different curves in each figure refer to, from bottom to top, d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$, $d_{3z^2-r^2}$ and s orbitals respectively.

(100) surface have a peak structure at E_F , whereas the orbital d_{yz} doesnot have that kind of structure. These features are in accordance with earlier calculations by Bullett et al. /92/. The s-band is rather featureless, however, the spike-like structures at the upper band edge are caused by the truncation procedure of the continued fraction coefficients.

4.4.2 Oxygen on Ni(100)

The calculated LDOS for chemisorbed oxygen on Ni(100) at different coverages are shown in Fig. 4.6. For p(2x2) structure the oxygen 2p-states form a band around 5.5 eV below E_F , whereas the 3d-electron LDOS is essentially unaffected by the oxygen 2p-states. Upon further increase of oxygen coverage, 2p-band broadens, its two dominant peaks get more separated and the oxygen 2p-electron DOS just above E_F increases. This can be understood due to the strong hybridization of oxygen 2p-states with nickel 4s-states and a relatively weaker hybridization with the 3d-states, the latter produces antibonding states just above E_F . Note, that the positions of the oxygen derived bonding and antibonding states in our calculation are in agreement with the measured oxygen derived peaks in photoemission /86/ and inverse photoemission /88,89/ spectroscopies. For p(1x1) overlayer structure these changes increase in the same direction, however, the band like features in oxygen 2p-states become more dominant. In order to exhibit more clearly the details of the changes in the LDOS upo chemisorption, we show in Fig 4.7 $\Delta \rho(E)$, which is the sum of the LDOS of the substrate nickel and adsorbate oxygen atoms subtracted from clean nickel LDOS. The features of this difference DOS, $\Delta \rho(E)$, around the Fermi energy is interesting. The

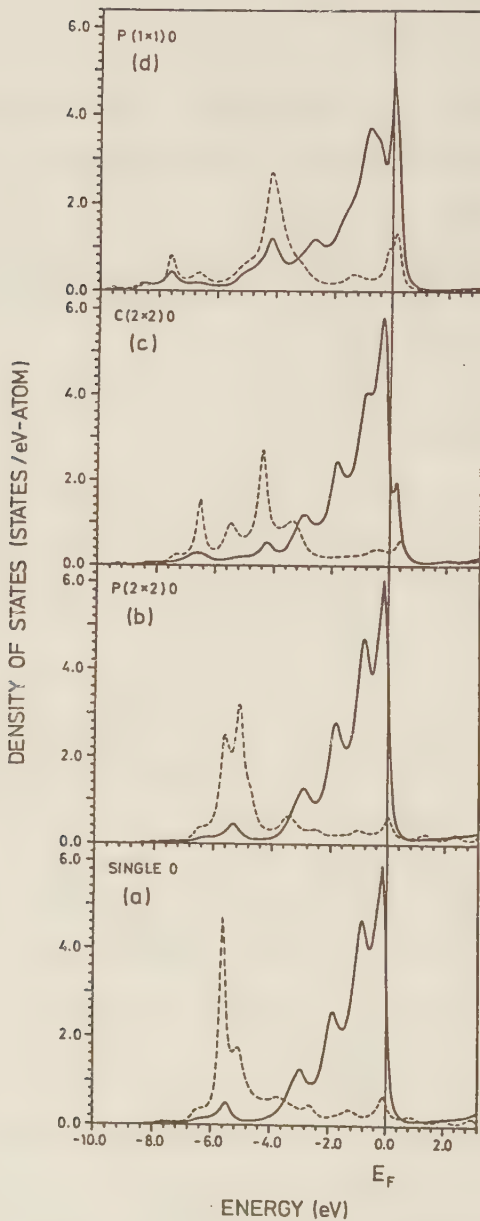


Fig. 4.6 : Local electronic density-of-states on oxygen (dashed line) and on neighboring nickel (full line) for (a) single adatom, (b) p(2x2), (c) c(2x2) and (d) p(1x1) overlayer structures.

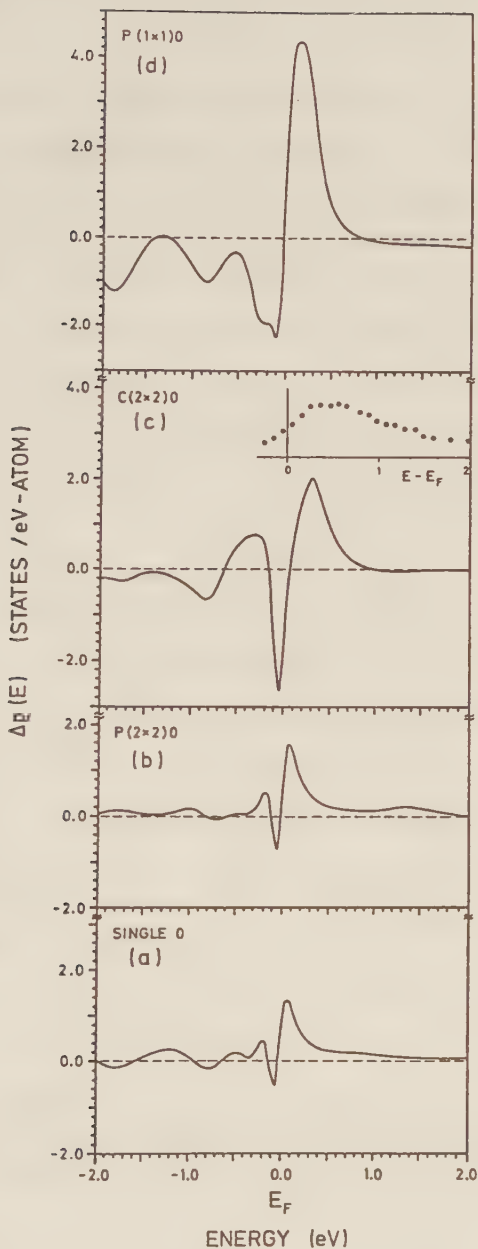


Fig. 4.7 : Difference in the density-of-states, $\Delta\rho(E)$, between oxygen covered and clean nickel for (a) single adatom, (b) p(2x2), (c) c(2x2) and (d) p(1x1) overlayer structures. The figure shown in inset in (c) refer to the inverse-photoemission difference spectra corresponding to a c(2x2) structure, Ref. /89/.

sharp dip just below E_F which increases with coverage is due to the nickel 3d electrons and indicates that upon chemisorption the 3d electron DOS of the substrate at E_F decreases. This is in accordance with experiments /86/ and other calculations. The peak structure in $\Delta \rho(E)$ just above E_F which grows rapidly with increasing coverage is due to antibonding oxygen 2p-states, as observed in inverse photoemission measurements /89/. For comparison the experimental results for a c(2x2) oxygen overlayer structure are also shown as inset in Fig. 4.7(c). Note, the peak position just above E_F is in good agreement with our calculation.

In Table 4.4 results are given for calculated electronic charge configurations and net transferred charge to oxygen for p(2x2), c(2x2) and p(1x1) overlayer structures, upon chemisorption.

Overlayer structure	Electronic configuration after chemisorption on:		Net transferred charge to Oxygen
	Nickel	Oxygen	
p(2x2)	3d ^{9.140} 4s ^{0.662}	2p ^{4.796}	0.796 (0.85)
c(2x2)	3d ^{8.842} 4s ^{0.710}	2p ^{4.894}	0.894 (1.05)
p(1x1)	3d ^{8.280} 4s ^{0.746}	2p ^{4.974}	0.974

Table 4.4: Calculated valence electronic configuration of Ni and O after chemisorption. Note, the starting configuration (before chemisorption) was 3d^{9.388} 4s^{0.611} (Ni) and 2p^{4.0} (O). The values given in bracket in the last column are from ref. /99/.

It is interesting to note that the Ni 3d charge decreases and its 4s charge increases slightly with increasing oxygen coverage. With increasing coverage nickel to oxygen charge transfer increases from

about 0.8 e to 1.0 e, which agree with ab-initio self-consistent calculations /99/. A large charge transfer to oxygen also gives an indication that upon chemisorption, the oxygen ionic radii increases appreciably to allow a possible overlap of its 2p orbitals at high coverages. This overlap will cause a repulsive interaction (close-shell type) between two neighboring oxygen atoms, decreasing thereby the binding energy of oxygen atoms with nickel at higher coverages. It should be recalled, that in NiO compound the transferred electronic charge to oxygen amounts to be 2 e. However, the transition from oxygen chemisorbed on Ni to the NiO will involve structural changes of the substrate lattice which will strongly affect the charge transfer. Since the Ni-Ni separation increases upon oxide formation by about 18%, one expects a shift of nickel 3d-states to lower binding energy and thereby causing an increase of the electronic charge transfer.

In Fig. 4.8 we show the binding energy of oxygen at different coverages calculated using eq. (4.18). The binding energy decreases first slowly, then more rapidly with increasing coverage. In view of our result we infer that for p(2x2) structure, with neighboring oxygen separation of $4.98 \text{ \AA}$, the indirect interactions are still negligible. For the c(2x2) structure, with oxygen separation of $3.52 \text{ \AA}$, the change in binding energy due to indirect repulsive interaction is still small. However, for the p(1x1) structure (with neighboring oxygen separation of $2.49 \text{ \AA}$) the binding energy decreases by about 10%.

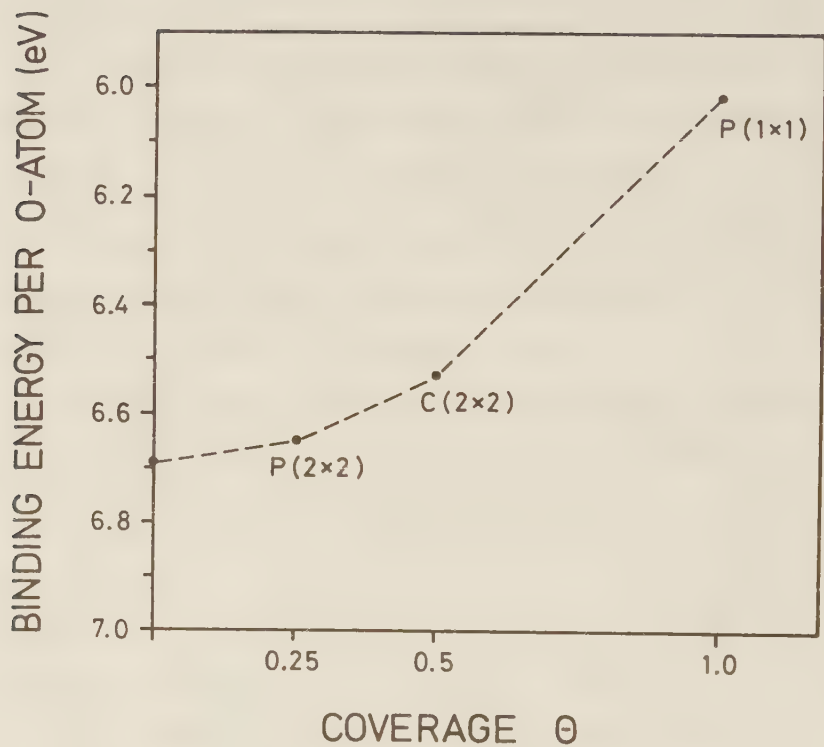


Fig. 4.8 : Calculated binding energy per oxygen atom, using eq. (4.18), as a function of coverage.

4.4.2.1 Repulsive interaction between oxygen at high coverages -

Our calculated binding energy of oxygen on Ni(100) indicates a decrease from 6.6 eV (single adatom) to about 6 eV at p(1x1) structure. Note, this decrease is caused due to the indirect interaction between oxygen atoms mediated through the substrate nickel. However, at high coverages the ionic radii of the chemisorbed oxygen increases, which is caused due to the extension of the radial part of the oxygen 2p orbital wave functions, and the neighboring oxygen 2p-orbitals overlap strongly causing a repulsion between them. Gallagher et al. /119/ have estimated this repulsion by calculating an optimum oxygen 2p orbital wave function and their overlap. They calculated the interaction energy between two oxygen atoms, assuming a closed shell repulsion, at distances corresponding to that in p(2x2), c(2x2) and p(1x1) structures and fitted with an exponential function. According to these authors, the interaction energy due to closed shell orbital overlap between two oxygen atoms situated on Ni(100) surface has a form,

$$E_{int}(r) = \frac{A}{r^6} + B \exp(-\beta r) \quad (4.19)$$

Here the first term is the Van der Waals attraction and the second term is the close shell repulsion due to the overlap of the oxygen 2p orbitals. Gallagher et al. obtained for O/Ni(100) system, $A = -76.7012 \text{ eV } \text{\AA}^6$, $B = 102.045 \text{ eV}$ and $\beta = 1.512 \text{ \AA}^{-1}$. Note, the repulsive term in Eq. (4.19) is obtained by assuming that the oxygen 2p orbital is completely full. But in our calculation we obtain the charge on oxygen 2p orbital to be 4.796 e, 4.894 e and 4.974 e for p(2x2), c(2x2) and p(1x1) structures respectively. We therefore

modify the repulsive term as $B' \exp(-\beta r)$, where $B' = f.B$ and f is the ratio of the actual 2p occupancy and the maximum 2p occupancy. In writing the repulsive term as above, we make the assumption that for an incomplete shell, as in our case, only the prefactor of the repulsive energy has to be modified, the exponent β being unchanged.

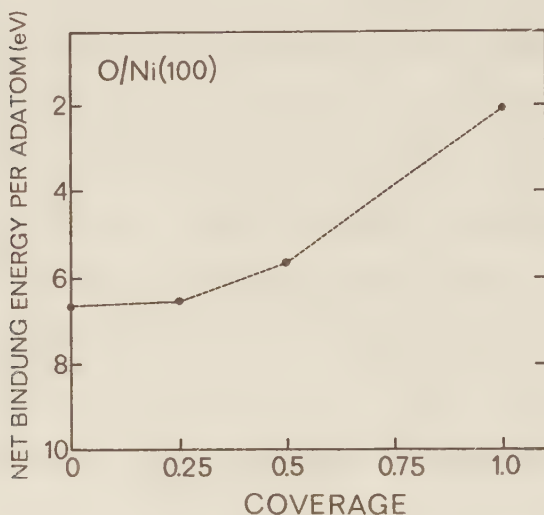


Fig. 4.9 : Net binding energy per oxygen atom, including the corrections made for the interaction due to direct overlap between their 2p orbitals, at different coverages.

Using this modified expression for the repulsive interaction, we obtain the decrease in the binding energy due to direct interaction between oxygen atoms to be 0.088 eV for p(2x2), 0.81 eV for c(2x2) and 3.92 eV for p(1x1) structures. In Fig. 4.9 we show the resultant binding energy for chemisorbed oxygen on Ni(100), including the corrections made for the interactions due to direct overlap between their 2p orbitals.

4.4.2.2 Formation of the overlayer structures and NiO -

The formation of different oxygen overlayer structures on Ni(100) can be well understood from our calculations. First, our calculated binding energy of 6.7 eV for single oxygen adatom clearly suggests that oxygen is dissociatively adsorbed (dissociation energy of $O_2 = 5.16$ eV /120/) on nickel (100) surface. At p(2x2) structure, binding energy decreases by about 0.1 eV (Fig. 4.8), which suggests that the adatom interactions are very small and the formation of a p(2x2) structure is possible. A decrease of binding energy of about 0.8 eV at c(2x2) structure, compared to that in p(2x2) structure, suggests why a p(2x2) structure is seen first in the LEED pattern /81/. Oxygen binding energy of about 2.1 eV at the p(1x1) structure explains that this is not formed, because, from energetic reasons, a p(1x1) oxygen coverage is endothermic relative to a c(2x2) plus half monolayer of oxygen. We have seen in earlier section that this large decrease in binding energy at p(1x1) structure is mainly caused due to strong repulsion between neighboring oxygen atoms. The kinetics of the growth of p(2x2) and c(2x2) structures would depend sensitively on temperature as the oxygen mobility rate decreases with decreasing temperature /37,38/.

Our calculated decrease in the oxygen binding energy with increasing coverage is important for understanding the penetration of oxygen atoms into the surface layer as occurs during the oxide formation process. One expects oxide formation to occur when it becomes energetically more favorable for the oxygen to sit inside on an interstitial nickel site than on a chemisorption site. Recent calculations by Chakraborty et al. /96/ obtain for the interstitial

oxygen binding energy 7.68 eV and for the binding energy of oxygen in NiO compound 7.97 eV. During the process of penetrating through the surface nickel layer, the oxygen atoms have to go through an energy barrier. This activation barrier is caused due to rigid nickel lattice which must get more distorted (expanded) to allow oxygen atoms to penetrate through it. The height and width of this activation barrier would sensitively depend on the perfection of the nickel surface and on temperature. For example, a defect or vacancy site (of substrate nickel) would allow the oxygen atoms to penetrate more easily than a geometrically perfect surface. We believe that increasing oxygen coverage would cause a distortion of the substrate nickel lattice, as by oxide formation the separation between neighboring nickel atoms increases by $\sim 18\%$. This offers an explanation why the observed oxidation process is delayed until a certain high local oxygen coverage has been established on the surface [37-38]. The temperature dependence of the oxidation rates (Fig. 1.5) can be understood in the following way. At low temperatures, due to less mobility, even a little oxygen exposure would lead to the formation of a local high coverage required to meet the oxidation activation barrier and oxidation nucleation would start. That is why one might not observe a complete $c(2 \times 2)$ structures at low temperatures. At relatively higher temperatures (~ 300 K), with increasing coverage oxygen will form, first a $p(2 \times 2)$ and then a $c(2 \times 2)$ structure. Upon further increase in oxygen coverage, the substrate nickel lattice will gradually get distorted to allow oxygen atoms to penetrate.

4.4.3 Results for S/Ni(100)

Results for LDOS of sulfur chemisorption on nickel (100) surface, for single adatom, p(2x2), c(2x2) and p(1x1) overlayer structures are shown in Fig. 4.10. We find, similar to oxygen, a sulfur derived peak at $\sim 4.5 - 5$ eV below E_F and an antibonding peak at ~ 1 eV above E_F . Our peak position below E_F is in quantitative agreement with photoemission data [105]. Note that sulfur 3p-states hybridize more strongly with nickel 3d band than oxygen 2p-states. Therefore, the antibonding sulfur peak is more pronounced. Furthermore, for p(1x1) structure the LDOS at nickel and sulfur sites completely modified.

Overlayer structure	Electronic configuration after chemisorption on		Net transferred charge to sulfur
	Nickel	Sulfur	
p(2x2)	3d ^{9.124} 4s ^{0.688}	3p ^{4.752}	0.752 (0.84)
c(2x2)	3d ^{8.893} 4s ^{0.734}	3p ^{4.746}	0.746 (0.72)

Table 4.5 : Calculated valence electronic configuration of Ni and S after chemisorption. Note, the starting configuration (before chemisorption) was 3d^{9.388} 4s^{0.611} (Ni) and 3p^{4.0} (S). The values given in bracket in the last column are from ref. [99].

In table 4.5 the valence electronic configurations after chemisorption and net transferred charge to sulfur is given for p(2x2) and c(2x2) overlayer structures. We note that the net transferred charge to sulfur decreases a little from p(2x2) to c(2x2) coverage, whereas for oxygen it showed an increasing trend (table 4.4). There

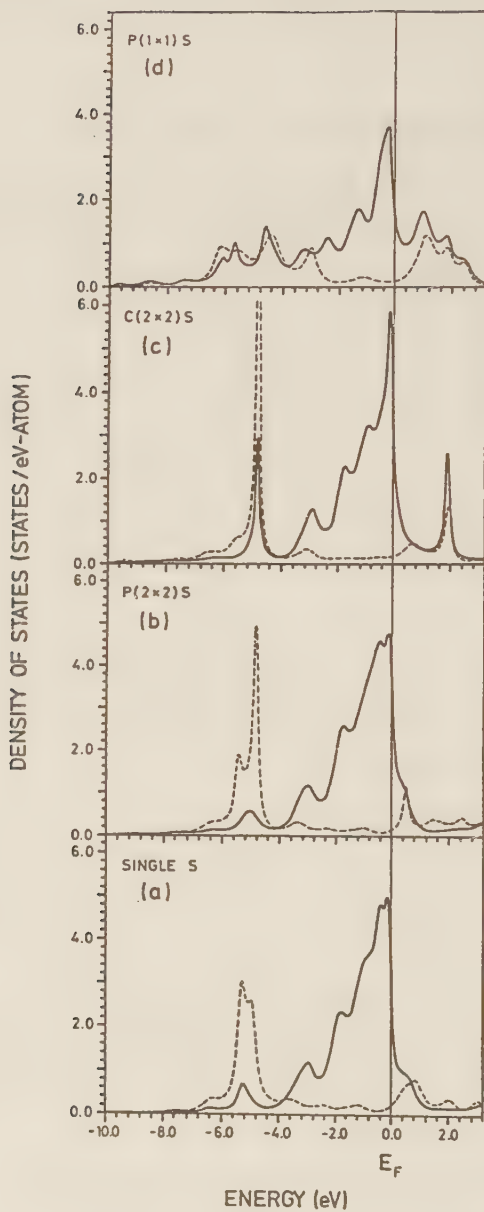


Fig. 4.10 : Local electronic density-of-states on sulfur (dashed line) and on neighboring nickel (full line) for (a) single adatom, (b) p(2x2), (c) c(2x2) and (d) p(1x1) overlayer structures.

can be several reasons for this. The electrostatic interaction between the anionic adsorbate and the substrate is part of the energetic advantage of the adsorbate ionicity. Since the distance between adsorbate and substrate atoms is larger for sulfur than for oxygen, this advantage is smaller for sulfur. Another reason could be connected with the repulsion between neighboring adsorbate atoms. As oxygen and sulfur atoms become more negatively charged, the overlap and hence the repulsion

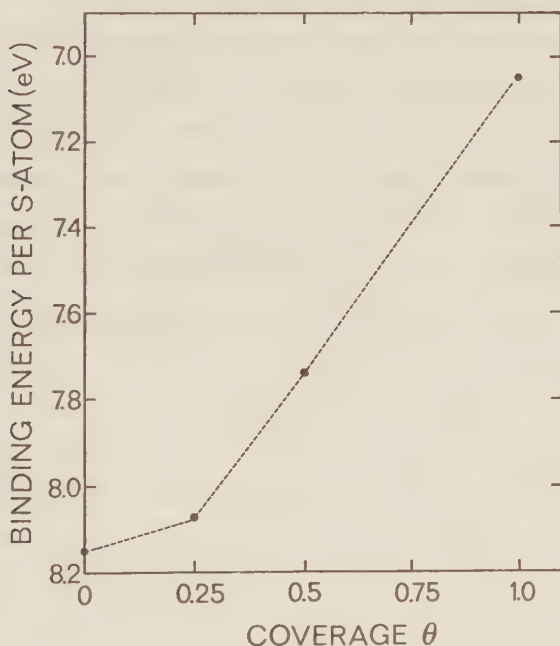


Fig. 4.11 : Calculated binding energy per sulfur atom as a function of coverage.

between adatoms increases. Since sulfur atom is larger in size than oxygen, this repulsion will rise more rapidly for S than for O.

In Fig. 4.11 we show the binding energy per sulfur atom, calculated using eq. (4.18). As expected, we find that the binding energy decreases with increasing coverage more rapidly for S than for O. Clearly, the indirect interactions for sulfur depends more strongly on coverage than that of oxygen. It should be noted that the calculated binding energy for sulfur as shown in Fig. 4.11 includes only indirect interactions between sulfur atoms mediated through the substrate nickel. However, it is possible to estimate the repulsion energy due to direct overlap of sulfur 3p wave function as done in oxygen case. But this will involve a calculation of effective wave function for 3p orbitals of chemisorbed sulfur and so far no such calculations exist. We would expect that this repulsion for sulfur will be more stronger than oxygen and thereby the compound forming tendencies might appear even at coverages less than 0.5 monolayer. The explanation of compound forming tendency for sulfur can be understood in the same light as for oxygen presented above.

5. CONCLUSIONS AND OUTLOOK

The work presented in this thesis covers a broad range of aspects of the surface properties of transition-metals and their alloys. In chapter 2 we have presented an electronic theory for surface segregation in transition-metal (d-band) alloys and calculated surface segregation in Cu-Ni alloys. Our calculation is based on a simple tight-binding theory taking d-electrons only, whereas effects of s-electrons and s-d hybridization are neglected. Furthermore, the alloy has been described in a Bethe-lattice, where the effects of the local environment are preserved irrespective of the long-range order in the system. Owing to these approximations, we obtained a simple and featureless form of the electronic density-of-states (DOS) for the alloy (Fig. 2.5). However, our calculated DOS spectra preserve the essential features of a more detailed calculation [59]. Our calculated surface composition for Cu-Ni alloy is in very good agreement with experiments at different temperatures. We have also predicted correctly the surface orientation dependent segregation and obtained a slightly more Cu segregation on more opened (100) surface than on closely packed (111) surface. Moreover, we have shown the importance of electron correlation effects in the segregation behavior

of Cu-Ni alloy, which has been neglected so far in theories of similar kind /52/. In the later section of chapter 2, we have presented a theory for the calculation of the surface core-level-shift (SCLS) of alloys which can be applied to alloys whose elements are neighbors in the periodic table, like Cu-Ni. The significance of the study of SCLS of alloys is to predict which element in the alloy segregates to the surface. The important fact about our analysis is that, for Cu-Ni alloy, the SCLS of Ni gives the heat of segregation of Cu to the surface. Unfortunately, experimental measurements of SCLS for alloys is still very limited; however, our calculated value agrees well with a recent measurement /20/ done for very low Cu concentration in Cu-Ni alloy. We believe that our calculation of SCLS will motivate further experimental studies of SCLS in alloys at various concentration range. The theory presented in chapter 2 can be extended to include s-d hybridization and magnetic effects and applied to study surface segregation to different alloys and also be used for studying segregation on stepped surfaces, interfaces etc.

In chapter 3, we have studied the effects of chemisorption, bulk absorption and sample size on the surface segregation behavior of binary alloys. Owing to its extremely simple form, we have used a bond type model with surface energies describing the surface segregation. It has been already shown /43,46,47/, and can also be seen from table 3.2, that this model gives a very good qualitative agreement of the segregation on clean surfaces of a large number of alloys including those with components of appreciably different molar volumes. In the case of chemisorption induced segregation, we find large effects only for those molecules which strongly bind only with one type of the alloy atoms. For example, this is the case for oxygen

or carbon-monoxide chemisorption on Cu-Ni alloys. While hydrogen chemisorption on the surface will not affect the surface segregation behavior of the alloy much, hydrogen absorption in the bulk can change the surface composition significantly. The case of surface segregation due to H absorption illustrates the essential features of segregation in ternary alloys, whereas the chemisorption induced surface segregation illustrates the features of segregation at interfaces.

The application of a bond model for calculating surface segregation in small clusters of binary alloys, presented in section 3.2, has yielded interesting results. First, we observe that the surface segregation behavior is strongly inhibited in alloy clusters compared to that in larger samples. Secondly, the shape dependent changes in surface segregation in alloy clusters (viz. icosahedral vs. cubooctahedral clusters) is significant for alloys with a moderate or low heat of segregation, for example, Au-Cu, Ag-Au, Ni-Pd etc. alloys. Our first conclusion serves an explanation for the alloy forming properties of bimetallic cluster-catalysts like Cu-Os and Cu-Ru, which show a very strong surface segregation of Cu in larger samples, making the formation of alloy impossible /6/. However, in small cluster samples, with dispersion 0.5 - 1, Cu-Ru and Cu-Os alloys show a moderate segregation of Cu which makes the alloy formation possible. This unique property of these alloys is key in the industrial application of Cu-Ru and Cu-Os alloy clusters as bimetallic cluster-catalysts /5/. Our second conclusion regarding the shape dependent changes for alloy clusters serves only a pathological purpose, as the experimental studies of segregation in alloy clusters are still very limited. However, we found that cubooctahedral alloy

cluster exhibits slightly more segregation compared to icosahedral one. This happens due to the fact that the surface of a cubooctahedron consists of (100) and (111) fcc facets, whereas icosahedron has only (111) facets (fig. 3.2) and the segregation at more opened (100) surface is slightly more than at (111) surface. In general, we found the bond model of segregation to be successful in explaining macroscopic segregation properties of alloy clusters, as was the case for the stability of neutral /78/ and charged /79,80/ metal clusters. This kind of model can be easily used in understanding segregation in ternary alloys, at the interfaces and grain boundaries etc.

In chapter 4, we have presented a detail calculation of the gas-surface interaction for oxygen and sulfur chemisorption on nickel (100) surface. The purpose of these calculations is twofold - first, to understand the mechanism of formation of $p(2 \times 2)$ and $c(2 \times 2)$ overlayer structures, and second, to present an understanding of the compound formation on nickel surface at higher adsorbate coverages. Our detail calculations, including explicitly 4s and 3d electrons and their hybridization for nickel and 2p electrons for oxygen (3p electrons for sulfur), have reproduced the essential details in the coverage dependent electronic structure of the substrate-adsorbate system, as observed in the photoemission and inverse photoemission measurements. We found the strong hybridization between adsorbate p and nickel 4s electrons to be very important in understanding the electronic structure. Calculated overage dependent binding energy is a first, but an essential, step towards the understanding of process of penetration of oxygen atoms into nickel surface as happens during oxide formation. It explains why the observed oxidation process is

delayed until a certain high local oxygen coverage has been established on the surface. For simplicity, we have not included the effect of lattice distortion as might be the case at high adatom coverage, and a calculation like that would give information about the activation barrier for oxidation. Detail calculations are also necessary for understanding the repulsion between adsorbate atoms at higher coverages.

APPENDIX A: EXPRESSION FOR DIAGONAL GREEN'S FUNCTION AT ALLOY SURFACE IN BETHE-LATTICE APPROXIMATION

In this appendix we derive the diagonal Green's function, used in Chapter 2, at the surface of a binary alloy $A_x B_{1-x}$ ($0 < x < 1$) using a Bethe-lattice description. In Bethe-lattice [121] model, a central atom or a cluster of atoms surrounding the central atom is treated exactly while the rest of the system is simulated by saturating the dangling bonds in the cluster with a Bethe-lattice. In this way, the effects of the local environment on the electronic density-of-states (DOS) are preserved irrespective of the long-range-order in the system. In the present description, of the alloy $A_x B_{1-x}$ at temperatures above the order-disorder transition temperature, only the short-range-order is of practical importance in determining the local electronic DOS.

For determining the LDOS at the surface, the alloy is described topologically by a mixed Bethe-lattice [19], shown schematically in Fig. A1.

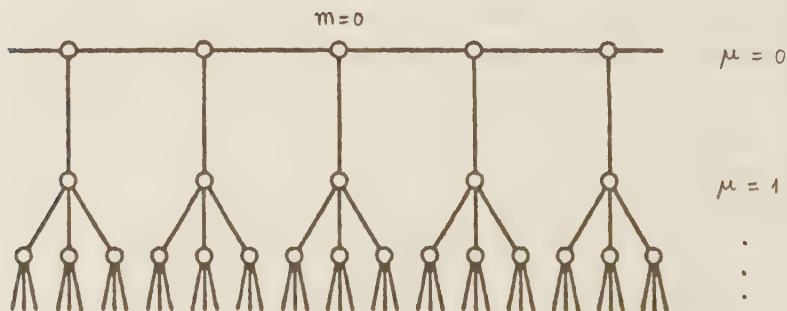


Fig. A1: Schematic representation of the mixed Bethe-lattice used in describing the surface of the alloy.

There are two kinds of atoms in the system: s (surface) and b (bulk). Any s atom is connected with Z_0 other s atoms and Z_1 b atoms, i.e., the surface coordination number is $Z_0 + Z_1$. Any b atom is connected with $Z_0 + 2Z_1$ other atoms. The average on-site energies of the d-band at the surface and in the bulk for the atom of type A(B) are denoted by $\epsilon_{A(B)}^s$ and $\epsilon_{A(B)}^b$ respectively. The electron hopping integral between the neighboring sites at the surface and in the bulk are denoted by t'_{IJ} and t_{IJ} respectively. t_{IJ} can have values t_{AA} , t_{BB} and t_{AB} . The matrix element of the Green's function between any two sites is denoted by $G_{\mu m, \nu n}(I \leftarrow J)$, where μ and ν denote planes on which atoms m and n are located respectively. The notation $I \leftarrow J$ means that atom of type I is at location μm , which has a parent atom of type J. The diagonal Green's function corresponding to atom A at the site $m=0$ at surface plane ($\mu=0$) obeys the following equation of motion,

$$\begin{aligned} (E - \epsilon_A^s) G_{00,00}(A) &= 1 + Z_0 \left[x_1 t'_{AA} G_{01,00}(A \leftarrow A) \right. \\ &\quad \left. + (1-x_1) t'_{AB} G_{01,00}(B \leftarrow A) \right] \\ &+ Z_1 \left[x t_{AA} G_{10,00}(A \leftarrow A) + (1-x) t_{AB} G_{10,00}(B \leftarrow A) \right] \quad (A1) \end{aligned}$$

Here x and x_1 denote the concentration of A-atom in the alloy, in bulk and surface respectively. Eq. (A1) can be rewritten as,

$$\begin{aligned} G_{00,00}(A) &= \left[E - \epsilon_A^s - Z_0 \left\{ x_1 t'_{AA} \alpha_1 + (1-x_1) t'_{AB} \alpha_3 \right\} \right. \\ &\quad \left. - Z_1 \left\{ x t_{AA} \beta_1 + (1-x) t_{AB} \beta_3 \right\} \right]^{-1} \quad (A2) \end{aligned}$$

and similarly for a B-atom at site $m=0$,

$$G_{00,00}(B) = \left[E - \epsilon_B^s - Z_0 \left\{ x_1 t'_{AB} \alpha_2 + (1-x_1) t'_{BB} \alpha_4 \right\} \right. \\ \left. - Z_1 \left\{ x t_{AB} \beta_2 + (1-x) t_{BB} \beta_4 \right\} \right]^{-1} \quad (A3)$$

Eqs. (A2) and (A3) are written in terms of two sets of transfer functions $(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$ and $(\beta_1, \beta_2, \beta_3, \beta_4)$ which are ratios of the Green's function at a particular site to that of its parent. The four components of each of those transfer functions depend upon whether the link is made via an A-A, A-B, B-A or B-B bond, and are given as,

$$\alpha_1 = \frac{G_{0n,00}(A \leftarrow A)}{G_{0n-1,00}(A \leftarrow I)}, \quad \alpha_2 = \frac{G_{0n,00}(A \leftarrow B)}{G_{0n-1,00}(B \leftarrow I)}$$

$$\alpha_3 = \frac{G_{0n,00}(B \leftarrow A)}{G_{0n-1,00}(A \leftarrow I)}, \quad \alpha_4 = \frac{G_{0n,00}(B \leftarrow B)}{G_{0n-1,00}(B \leftarrow I)}$$

and

$$\beta_1 = \frac{G_{\mu n,00}(A \leftarrow A)}{G_{\mu-1 n,00}(A \leftarrow I)}, \quad \beta_2 = \frac{G_{\mu n,00}(A \leftarrow B)}{G_{\mu-1 n,00}(B \leftarrow I)}$$

$$\beta_3 = \frac{G_{\mu n,00}(B \leftarrow A)}{G_{\mu-1 n,00}(A \leftarrow I)}, \quad \beta_4 = \frac{G_{\mu n,00}(B \leftarrow B)}{G_{\mu-1 n,00}(B \leftarrow I)}$$

$$\mu \geq 1, \quad n \geq 1$$

The equations of motion satisfied by α 's and β 's can be obtained from a straightforward generalisation of Eq. (A1), written for off-diagonal matrix element of the Green's function, and are given by,

$$\alpha_1 = t'_{AA} \left[E - \epsilon_A^S - (Z_0 - 1) \left\{ x_1 t'_{AA} \alpha_1 + (1-x_1) t'_{AB} \alpha_3 \right\} - Z_1 \left\{ x t_{AA} \beta_1 + (1-x) t_{AB} \beta_3 \right\} \right]^{-1}$$

$$\alpha_2 = (t'_{AB} / t'_{AA}) \alpha_1 \quad (A4)$$

$$\alpha_3 = t'_{AB} \left[E - \epsilon_B^S - (Z_0 - 1) \left\{ x_1 t'_{AB} \alpha_2 + (1-x_1) t'_{BB} \alpha_4 \right\} - Z_1 \left\{ x t_{AB} \beta_2 + (1-x) t_{BB} \beta_4 \right\} \right]^{-1}$$

$$\alpha_4 = (t'_{BB} / t'_{AB}) \alpha_3$$

and

$$\beta_1 = t_{AA} \left[E - \epsilon_A^b - (Z_1 - 1) \left\{ x t_{AA} \gamma_1 + (1-x) t_{AB} \gamma_3 \right\} + (Z_0 + Z_1) \left\{ x t_{AA} \delta_1 + (1-x) t_{AB} \delta_3 \right\} \right]^{-1}$$

$$\beta_2 = (t_{AB} / t_{AA}) \beta_1 \quad (A5)$$

$$\beta_3 = t_{AB} \left[E - \epsilon_B^b - (Z_1 - 1) \left\{ x t_{AB} \gamma_2 + (1-x) t_{BB} \gamma_4 \right\} + (Z_0 + Z_1) \left\{ x t_{AB} \delta_2 + (1-x) t_{BB} \delta_4 \right\} \right]^{-1}$$

$$\beta_4 = (t_{BB} / t_{AB}) \beta_3$$

The sets of transfer functions ($\gamma_1, \gamma_2, \gamma_3, \gamma_4$), describing the ratio of Green's functions between a surface and a bulk atom are given by,

$$\gamma_1 = t_{AA} \left[E - \epsilon_A^s - Z_0 \left\{ x_1 t'_{AA} \alpha_1 + (1-x_1) t'_{AB} \alpha_3 \right\} - (Z_1 - 1) \left\{ x t_{AA} \beta_1 + (1-x) t_{AB} \beta_3 \right\} \right]^{-1}$$

$$\gamma_2 = (t_{AB} / t_{AA}) \gamma_1 \quad (A6)$$

$$\gamma_3 = t_{AB} \left[E - \epsilon_B^s - Z_0 \left\{ x_1 t'_{AB} \alpha_2 + (1-x_1) t'_{BB} \alpha_4 \right\} - (Z_1 - 1) \left\{ x t_{AB} \beta_2 + (1-x) t_{BB} \beta_4 \right\} \right]^{-1}$$

$$\gamma_4 = (t_{BB} / t_{AB}) \gamma_3$$

The final set of transfer functions describing the ratio of Green's function only between bulk atoms is written as,

$$\delta_1 = t_{AA} \left[E - \epsilon_A^b - (Z-1) \left\{ x t_{AA} \delta_1 + (1-x) t_{AB} \delta_3 \right\} \right]^{-1}$$

$$\delta_2 = t_{AB} \left[E - \epsilon_A^b - (Z-1) \left\{ x t_{AA} \delta_1 + (1-x) t_{AB} \delta_3 \right\} \right]^{-1}$$

$$\delta_3 = t_{AB} \left[E - \epsilon_B^b - (Z-1) \left\{ x t_{AB} \delta_3 + (1-x) t_{BB} \delta_4 \right\} \right]^{-1}$$

$$\delta_4 = t_{BB} \left[E - \epsilon_B^b - (Z-1) \left\{ x t_{AB} \delta_3 + (1-x) t_{BB} \delta_4 \right\} \right]^{-1} \quad (A7)$$

Eqs. (A4)-(A7) have to be solved simultaneously for obtaining the diagonal Green's function (Eq. (A2) and (A3)). For this, we first solved iteratively the set of bulk transfer functions. We used the Newton-Raphson /122/ method for the iterative process and obtained convergence upto a very high degree ($< 10^{-6}$). These converged set of δ 's were used in Eq. (A5), which together with Eqs. (A4) and (A6)

was solved iteratively.

The diagonal Green's functions for bulk atoms in the alloy are given by,

$$G_{00}^{bulk}(A) = \left[E - \epsilon_A^b - Z \left\{ x t_{AA} \delta_1 + (1-x) t_{AB} \delta_3 \right\} \right]^{-1} \quad (A8)$$

and

$$G_{00}^{bulk}(B) = \left[E - \epsilon_B^b - Z \left\{ x t_{AB} \delta_2 + (1-x) t_{BB} \delta_4 \right\} \right]^{-1} \quad (A9)$$

Eqs. (A2), (A3) and (A8), (A9) are used in eq. (2.8) to calculate local electronic density-of-states at surface and bulk respectively.

APPENDIX B: ELEMENTS OF THE RECURSION METHOD FOR CALCULATING THE LOCAL DENSITY-OF-STATES

In this appendix we discuss in brief the 'recursion method' for the calculation of the local density-of-states (LDOS) $\rho_{i,\alpha}(E)$, in relation to a set of atomic orbitals $|i,\alpha\rangle$. The recursion method /109,110/ involves in setting up a new orthonormal basis set $\{u_n\}$, in such a way that the Hamiltonian matrix has a tridiagonal form in this new basis set. This can be achieved by constructing the orbitals $|u_n\rangle$ ($n = 0, 1, \dots$) of the new basis set, from the old basis set $|i,\alpha\rangle$, such that each new orbital interacts only with its preceding and following orbitals. It should be recalled that in the tight-binding approximation the orbitals $|i,\alpha\rangle$, corresponding to an orbital α for an atom situated at site i , form a set of Wannier functions so that the Hamiltonian matrix has a sparse form. Now, the first element of the new basis set $|u_0\rangle$ is chosen to be equal to a particular orbital $|i,\alpha\rangle$, on which we want to calculate the LDOS. The other orbitals in the orthonormal basis set are generated using the relation,

$$b_{n+1} |u_{n+1}\rangle = H |u_n\rangle - a_n |u_n\rangle - b_n |u_{n-1}\rangle \quad (B1)$$

Here a_n, b_n are numerical coefficients. Suppose $|u_0\rangle \equiv |i,\alpha\rangle$ is localized on the central atom shown in Fig. B1. The Hamiltonian H in Eq. B1 is a matrix connecting $|u_0\rangle$ with the orbital $|u_1\rangle$ on nearby atoms (e.g. nearest and next-nearest neighbor atoms). According to Eq. B1, $H |u_0\rangle$ generates an extended orbital $|u_1\rangle$ spreading over these neighbors.

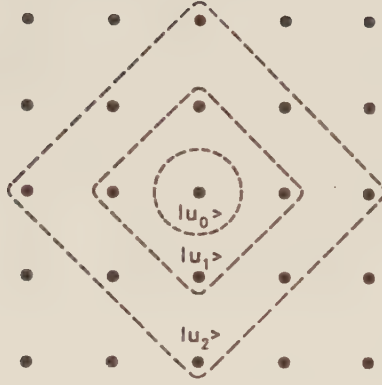


Fig. B1: Illustration of the regions, marked by dashed line, covered by the new basis orbitals $|u_0\rangle$, $|u_1\rangle$, $|u_2\rangle$ etc.

Similarly, $H |u_1\rangle$ and hence $|u_2\rangle$ in Eq. B1 extends over the neighbors of the neighbors included in $|u_1\rangle$. Thus $|u_1\rangle$, $|u_2\rangle$, $|u_3\rangle$, etc. spread out further and further away (Fig. B1) from the central orbital $|u_0\rangle$ whose LDOS is to be calculated. The coefficients a_n and b_n are defined as follows,

$$a_n = \langle u_n | H | u_n \rangle$$

and

$$b_n = \langle u_{n-1} | H | u_n \rangle = \langle u_n | H | u_{n-1} \rangle$$

$$\langle u_n | H | u_m \rangle = 0, \text{ otherwise.}$$

Thus, in the new basis set, the Hamiltonian matrix has following

tridiagonal form,

$$[H] = \begin{bmatrix} a_0 & b_1 & 0 & 0 & 0 & 0 & 0 & . & . & . \\ b_1 & a_1 & b_2 & 0 & 0 & 0 & 0 & . & . & . \\ 0 & b_2 & a_2 & b_3 & 0 & 0 & 0 & . & . & . \\ 0 & 0 & \dots & \dots & \dots & 0 & 0 & . & . & . \\ . & . & . & . & . & . & . & . & . & . \end{bmatrix} \quad (B3)$$

The diagonal element of the Green's function $G(E)$ is given by,

$$\langle i, \alpha | G(E) | i, \alpha \rangle = \langle u_0 | (E - H)^{-1} | u_0 \rangle \quad (B4)$$

The matrix $[E - H]$ is given by,

$$[E - H] = \begin{bmatrix} (E - a_0) & -b_1 & 0 & 0 & . \\ -b_1 & (E - a_1) & -b_2 & 0 & . \\ 0 & -b_2 & (E - a_3) & -b_3 & . \\ . & . & \dots & \dots & \dots \end{bmatrix} \quad (B5)$$

The first diagonal element of the inverse of the matrix (B5) can be expressed as,

$$\langle u_0 | [E - H]^{-1} | u_0 \rangle = \det | D_0 | / \det | D_1 |, \quad (B6)$$

where D_0 is the whole determinant of the matrix $[E - H]$ and D_1 is the same with the first row and column removed. From the Cauchy expansion /123/ of a determinant one can write,

[illegible]

Here, D_n refers to a determinant of the matrix $[E - H]$ (Eq. B5) with first n rows and columns missing.

Substituting eqs. B7 in B4, the diagonal Green's function can be written as a continued fraction,

$$\langle i, \alpha | G(E) | i, \alpha \rangle = \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{E - a_2 - \frac{b_3^2}{E - \dots}}}} \quad (B8)$$

The local electronic density-of-states at the central site is given as,

$$\rho_{i\alpha}(E) = - (1/\pi) \text{Im} \langle i, \alpha | G(E) | i, \alpha \rangle \quad (\text{B9})$$

Thus, once the tridiagonal coefficients a_i, b_i are determined, the LDOS, at the site and orbital concerned, can be easily evaluated. In practical uses, one calculates only a finite number of coefficients (say, upto n levels) depending upon the size of the cluster used to describe the crystal, which is ultimately limited by computer storage capacity. It should be noted, that the successive deeper levels in the continued fraction in eq. B8 describe the contributions to the LDOS from increasingly distant atoms from the central atom (Fig. B1). If after n levels in the continued fraction we set all $a_i = a$ and $b_i = b$, then the remainder of the continued fraction in (B8) can be written as,

$$t(E) = \frac{b}{E - a - t(E)} \quad (B10)$$

Eq. B10 gives the so called square root terminator /109/ of the continued fraction, which can be easily solved for $t(E)$ as,

$$t(E) = (1/2) \left[E - a \pm \sqrt{(E - a)^2 - 4 b^2} \right] \quad (B11)$$

Clearly, the band continuum of states will lie in the energy range,

$$a - 2 b < E < a + 2 b$$

The square root terminator, given by eq. B10, is only suitable when there is no gaps in the LDOS spectrum and when the band edges are known a priori. However, if the band edges are not known then an ad hoc choice of the terminating coefficients a, b can lead to some

problems. For example, if the band width is chosen to be too small, then the LDOS develops spurious peaks at the band edges and some weight may be lost from the band by delta function like states splitting off from the band edges. If a band width is chosen which is too large, then tails with negligible weight are pulled out from the LDOS spectra to the edges. In order to avoid these difficulties, a new scheme has been proposed recently by Beer and Pettifor /114/, in which the actual band edges are calculated from a finite set of continued fractions a_n, b_n . This method makes use of the fact that the diagonal Green's function $G_{i\alpha, i\alpha}(E)$ must diverge simultaneously at the top and bottom of the band, so that the delta functions which would carry weight away from the band must be situated exactly at the band edges.

From eq. B10, we get at the band edges,

$$t(a \pm 2b) = \pm b \quad (B12)$$

Therefore, at the band edges ($E = a \pm 2b$), we get from eq. B8, a finite continued fraction,

$$G_{i\alpha, i\alpha}(a \pm 2b) = \frac{(1/2)}{\pm b - (1/2)(a_0 - a) - (1/4)b_1^2} \quad (B13)$$

$$\frac{1}{\pm b - (1/2)(a_1 - a) - (1/4)b_2^2}$$

$$\frac{\dots\dots\dots}{(1/2)b_n^2}$$

$$\pm b - (a_n - a)$$

Thus for a given value of a , the eigenvalues of the following $(n+1) \times (n+1)$ tridiagonal matrix,

$$\begin{bmatrix} \frac{1}{2}(a_0 - a) & \frac{1}{2}b_1 & 0 & . & . & 0 & 0 \\ \frac{1}{2}b_1 & \frac{1}{2}(a_1 - a) & b & . & . & 0 & 0 \\ 0 & \dots & \dots & \dots & . & 0 & 0 \\ . & . & . & . & . & . & . \\ 0 & 0 & 0 & . & . & \frac{1}{2}(a_{n-1} - a) & (1/\sqrt{2})b_n \\ 0 & 0 & 0 & . & . & (1/\sqrt{2})b_n & (a_n - a) \end{bmatrix} \quad (B14)$$

are those values of b for which $G_{i\alpha, i\alpha}$ ($a \pm 2b$) diverges. The maximum and minimum eigenvalues are those values of b for which no delta function has split off from the top and bottom of the band respectively. The magnitudes of the maximum and minimum eigenvalues of b are same, and is taken to be the terminating value of b . Beer and Pettifor /114/ have shown that the LDOS obtained using this terminating scheme preserves all essential features even at the band edges, in comparison to a different approximation due to Nex /124/. In our calculations, we used the Beer and Pettifor scheme for the termination of continued fraction.

APPENDIX C : EXPRESSION FOR THE CHANGE IN COULOMB AND EXCHANGE-CORRELATION ENERGIES DUE TO CHEMISORPTION

In this appendix we derive an expression for the change in the Coulomb and exchange-correlation energies, which is counted twice in the binding energy expression Eq. (4.11). The correction in the energy due to chemisorption is written as,

$$\Delta E_{\text{corr}} = \frac{1}{2} (\Delta E_{\text{coul}} + \Delta E_{\text{xc}}) \quad (\text{C1})$$

where,

$$\Delta E_{\text{coul}} = \Delta \sum_{\substack{i \neq j \\ \alpha, \beta}} \iint d^3 \underline{r} d^3 \underline{r}' \frac{n_{i\alpha}(\underline{r}) n_{j\beta}(\underline{r}')}{|\underline{r} - \underline{r}'|} \quad (\text{C2})$$

and

$$\Delta E_{\text{xc}} = \Delta \sum_{i, \alpha} \int d^3 \underline{r} n_{i\alpha}(\underline{r}) \varepsilon_{\text{xc}}[n_{i\alpha}(\underline{r})] \quad (\text{C3})$$

Here $n_{i\alpha}(\underline{r})$ is the charge-density associated with the orbital α at site i , $\varepsilon_{\text{xc}}[n_{i\alpha}(\underline{r})]$ in Eq. C3 is the exchange-correlation energy density and the changes refer to that between after and before chemisorption.

Let us first examine Eq. C2, which can be simplified to the form,

$$\begin{aligned} \Delta E_{\text{coul}} = \sum_{\substack{i \neq j \\ \alpha, \beta}} \iint d^3 \underline{r} d^3 \underline{r}' & \left[\frac{\Delta n_{i\alpha}(\underline{r})}{|\underline{r} - \underline{r}'|} \{ n_{j\beta}(\underline{r}') + \Delta n_{j\beta}(\underline{r}') \} \right. \\ & \left. + \frac{\Delta n_{j\beta}(\underline{r}')}{|\underline{r} - \underline{r}'|} n_{i\alpha}(\underline{r}) \right] \quad (\text{C4}) \end{aligned}$$

In writing eq. (C4) from eq. (C2), we have used the following identity,

$$\Delta \left[n_{i\alpha}(\underline{r}) n_{j\beta}(\underline{r}') \right] = \Delta n_{i\alpha}(\underline{r}) \left(n_{j\beta}(\underline{r}') + \Delta n_{j\beta}(\underline{r}') \right) + n_{i\alpha}(\underline{r}) \Delta n_{j\beta}(\underline{r})$$

The change in the Hartree potential at site $\underline{r}$ is written as,

$$\Delta V_H(\underline{r}) = \sum_{i,\alpha} \int d^3 \underline{r}' \frac{\Delta n_{i\alpha}(\underline{r}')}{|\underline{r} - \underline{r}'|} \quad (C5)$$

Using eq. C5, eq. C4 can be written as,

$$\begin{aligned} \Delta E_{coul} = & \sum_{j\beta} \int d^3 \underline{r}' \Delta V_{H,j\beta}(\underline{r}') \tilde{n}_{j\beta}(\underline{r}') \\ & + \sum_{i\alpha} \int d^3 \underline{r} \Delta V_{H,i\alpha}(\underline{r}) n_{i\alpha}(\underline{r}) \end{aligned} \quad (C6)$$

where $\tilde{n}_{j\beta} = n_{j\beta} + \Delta n_{j\beta}$ is the charge density associated with the orbital β at site j after chemisorption. Now, neglecting the variation of ΔV_H within the Wigner-Seitz cell, we obtain,

$$\Delta E_{coul} = \sum_{i\alpha} \Delta V_{H,i\alpha} (\tilde{N}_{i\alpha} + N_{i\alpha}) \quad (C7)$$

where, $N_{i\alpha} = \int d^3 \underline{r} n_{i\alpha}(\underline{r})$ is the total charge associated with the orbital α at site i .

Now, let us examine the exchange-correlation term given by eq. (C3) and let us for the time being drop the indices i, α . Using the Slater's [11] form for the exchange-correlation potential,

$$V_{xc} = \alpha \cdot n^{1/3} \quad (C8)$$

and the exchange-correlation energy density,

$$\varepsilon_{xc} [n(r)] = \frac{3}{4} \alpha n^{1/3} \quad (C9)$$

the exchange-correlation energy of the system can be written as,

$$E_{xc} = \frac{3}{4} \alpha \int d^3 \underline{r} [n(\underline{r})]^{4/3} \quad (C10)$$

Therefore, the change in E_{xc} due to chemisorption,

$$\begin{aligned} \Delta E_{xc} &= \frac{3}{4} \alpha \int d^3 \underline{r} \Delta [n(\underline{r})]^{4/3} \\ &= \alpha \int d^3 \underline{r} \left[n^{1/3} \Delta n + \frac{1}{6} n^{-2/3} (\Delta n)^2 \right] \quad (C11) \\ &\quad \text{with terms upto } (\Delta n)^2 \end{aligned}$$

Now, from eq. (C8) we have,

$$\Delta V_{xc} = \alpha (\Delta n^{1/3}) = \frac{\alpha}{3} \left[n^{-2/3} \Delta n - \frac{1}{3} n^{-5/3} (\Delta n)^2 \right]$$

$$\text{i.e., } \Delta n \Delta V_{xc} = \frac{\alpha}{3} n^{-2/3} (\Delta n)^2 \quad \text{with terms upto } (\Delta n)^2 \quad (C12)$$

$$\text{and } n \Delta V_{xc} = \frac{\alpha}{3} \left[n^{1/3} \Delta n - \frac{1}{3} n^{-2/3} (\Delta n)^2 \right] \quad (C13)$$

Now, using the identities (C12) and (C13), eq. (C11) can be written as,

$$\begin{aligned} \Delta E_{xc} &= \int d^3 \underline{r} \left(3 n \Delta V_{xc} + \frac{3}{2} \Delta n \Delta V_{xc} \right) \\ &= \frac{3}{2} \Delta V_{xc} (\tilde{N} + N) \end{aligned}$$

where, $\tilde{N} = N + \Delta N$

Therefore, the total change in the exchange-correlation energy due to all orbitals is,

$$\Delta E_{xc} = \frac{3}{2} \sum_{i,\alpha} \Delta V_{xc,i\alpha} (\tilde{N}_{i\alpha} + N_{i\alpha}) \quad (C14)$$

So the correction term in the energy can be written as,

$$\Delta E_{corr} = \frac{1}{2} \sum_{i\alpha} \left(\Delta V_{H,i\alpha} + \frac{3}{2} \Delta V_{xc,i\alpha} \right) (\tilde{N}_{i\alpha} + N_{i\alpha}) \quad (C15)$$

Now, if we define the mean energies (first moment) of the valence band density-of-states as,

$$C_{i\alpha} = \int_{-\infty}^{+\infty} E \rho_{i\alpha}(E) dE, \quad \tilde{C}_{i\alpha} = \int_{-\infty}^{+\infty} E \tilde{\rho}_{i\alpha}(E) dE$$

then,
$$\Delta C_{i\alpha} = \tilde{C}_{i\alpha} - C_{i\alpha} \equiv \Delta V_{H,i\alpha} + \Delta V_{xc,i\alpha} \quad (C16)$$

In other words, the change in total energy of the full band is equal to the change in the potential energies, the kinetic energy part being zero. So, the eq. (C15) can be written as,

$$\Delta E_{corr} \simeq \frac{1}{2} \sum_{i\alpha} \Delta C_{i\alpha} (\tilde{N}_{i\alpha} + N_{i\alpha}) \quad (C17)$$

It should be noted that in writing eq. (C17), the factor 3/2 before ΔV_{xc} in eq. (C15) has been dropped. This is an approximation and can be valid as ΔV_{xc} due to chemisorption is rather small [125]. Eq. (C17) is used in chemisorption binding energy expression Eq. (4.11).

REFERENCES :

1. J. E. Inglesfield and B. W. Holland, in The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Vol. 1, eds. D. A. King and D. P. Woodruff, (Elsevier, Amsterdam, 1981), pp. 183-355, and references therein.
2. G. Allan, in Handbook of Surfaces and Interfaces, Vol. 1, ed. L. Dobrzynski, (Garland STPM, New York and London, 1978), pp. 299-416.
3. V. Ponec, Surf. Sci. **80**, 352 (1979).
4. W. M. H. Sachtler and R. A. van Santen, Appl. Surf. Sci. **3**, 121 (1979).
5. J. H. Sinfelt, Rev. Mod. Phys. **51**, 569 (1979).
6. J. H. Sinfelt, Y. L. Lam, J. A. Cusumano and A. E. Barnett, J. Catal. **42**, 227 (1976).
7. J. H. Sinfelt, J. Catal. **29**, 308 (1973).
8. J. H. Sinfelt, J. L. Carter and D. J. C. Yates, J. Catal. **24**, 283 (1972).
9. C. R. Helms and K. Y. Yu, J. Vac. Sci. Technol. **12**, 276 (1975).
10. K. Watanabe, M. Hashiba and T. Yamashita, Surf. Sci. **61**, 483 (1976).
11. H. H. Brongersma and T. M. Buck, Surf. Sci. **53**, 649 (1975).
12. H. H. Brongersma, M. J. Sparnaay and T. M. Buck, Surf. Sci. **71**, 657 (1978).
13. Y. S. Ng, T. T. Tsong and S. B. McLane Jr., Phys. Rev. Lett. **42**, 588 (1979).
14. K. Wandelt and C. R. Brundle, Phys. Rev. Lett. **46**, 1529 (1981).
15. B. Johansson and N. Mårtensson, Phys. Rev. B **21**, 4427 (1980).
16. A. Rosengren and B. Johansson, Phys. Rev. B **23**, 3852 (1981).
17. P. Steiner and S. Hüfner, Solid St. Commun. **37**, 279 (1981).
18. V. Kumar, D. Tománek and K. H. Bennemann, Solid St. Commun. **39**, 987 (1981).
19. S. Mukherjee, J. L. Morán-López, V. Kumar and K. H. Bennemann, Phys. Rev. B **25**, 730 (1982).
20. W. F. Egelhoff Jr., Phys. Rev. Lett. **50**, 587 (1983).
21. C. R. Helms, in Interfacial Segregation, eds. W. C. Johnson and J. M. Blakely. (American Society for Metals, Ohio, 1979), p. 175.

22. M. Hansen, Constituents of binary alloys, (McGraw Hill, New York, 1958).
23. I. Toyoshima and G. A. Somorjai, *Catal. Rev. Sci. Eng.* 19, 105 (1979).
24. K. Y. Yu, D. T. Ling and W. E. Spicer, *J. Catal.* 44, 373 (1976).
25. J. C. M. Harberts, A. F. Bourgonje, J. J. Stephan and V. Ponec, *J. Catal.* 47, 92 (1977).
26. G. Ertl and J. Küppers, *Surf. Sci.* 24, 104 (1971).
27. Y. Takasu, Y. Matsuda, S. Maru, N. Hayashi, H. Yoneyama and H. Tamura, *J. Phys. Chem.* 79, 1480 (1975).
28. J. J. Burton, C. R. Helms and R. S. Polizzotti, *J. Chem. Phys.* 65, 1085 (1976); *Surf. Sci.* 57, 425 (1976); *J. Vac. Sci. Technol.* 13, 204 (1976).
29. F. L. Williams and M. Boudart, *J. Catal.* 30, 438 (1973).
30. D. Brennan, D. O. Hayward and B. M. W. Trapnell, *Proc. R. Soc. (London)*, A256, 81 (1960).
31. D. Brennan and M. J. Graham, *Discuss. Faraday Soc.* 41, 95 (1966).
32. D. F. Klemperer and F. S. Stone, *Proc. R. Soc. (London)*, A243, 375 (1957).
33. G. Wedler, *Z. Phys. Chem.* 24, 73 (1960).
34. P. H. Holloway and J. B. Hudson, *Surf. Sci.* 43, 123 (1974).
35. P. H. Holloway and J. B. Hudson, *Surf. Sci.* 43, 141 (1974).
36. P. H. Holloway, *J. Vac. Sci. Technol.* 18, 653 (1981).
37. C. R. Brundle and H. Hopster, *J. Vac. Sci. Technol.* 18, 663 (1981).
38. C. R. Brundle, in Aspects of the kinetics and dynamics of surface reactions, ed. U. Landman (American Inst. of Physics, New York, 1980).
39. F. L. Williams and D. Nason, *Surf. Sci.* 45, 377 (1974).
40. R. A. Van Santen and W. M. H. Sachtler, *J. Catal.* 33, 202 (1974).
41. J. L. Morán-López and K. H. Bennemann, *Phys. Rev. B* 15, 4769 (1977).
42. D. Kumar, A. Mookerjee and V. Kumar, *J. Phys. F* 6, 725 (1976).
43. A. R. Miedema, *Z. Metallkd.* 69, 455 (1978).
44. P. Wynblatt and R. C. Ku, *Surf. Sci.* 65, 511 (1977).

45. V. Kumar, Phys. Rev. B 23, 3576 (1981).
46. J. C. Hamilton, Phys. Rev. Lett. 42, 989 (1979).
47. J. R. Chelikowsky, Surf. Sci. 139, L197 (1984).
48. F. F. Abrahams, N. H. Tsai and G. M. Pound, Surf. Sci. 83, 406 (1979).
49. V. Kumar, Surf. Sci. 84, L231 (1979).
50. J. L. Morán-López and L. M. Falicov, Phys. Rev. B 18, 2542 (1978).
51. J. L. Morán-López and L. M. Falicov, Phys. Rev. B 18, 2549 (1978).
52. G. Kerker, J. L. Morán-López and K. H. Bennemann, Phys. Rev. B 15, 638 (1977).
53. P. Lambin and J. P. Gaspard, J. Phys. F 10, 2413 (1980).
54. C. A. Balseiro and J. L. Morán-López, Phys. Rev. B 21, 349 (1980).
55. M. Robbins and L. M. Falicov, Phys. Rev. B 25, 2343 (1982).
56. M. Robbins and L. M. Falicov, Phys. Rev. B 29, 1333 (1984).
57. R. Riedinger and H. Dreysse, Phys. Rev. B 27, 2073 (1983).
58. H. Dreysse and R. Riedinger, Phys. Rev. B 28, 5669 (1983).
59. G. M. Stocks, R. W. Williams and J. S. Faulkner, Phys. Rev. B 4, 4390 (1971).
60. P. Heimann, H. Neddermeyer and M. Pessa, Phys. Rev. 17, 427 (1978).
61. P. H. Citrin and G. K. Wertheim, Phys. Rev. 27, 3176 (1983).
62. M. Desjonqueres, D. Spanaard, Y. Lassailly and C. Guillot, Solid St. Commun. 34, 807 (1980).
63. A. R. Miedema, Z. Metallkd. 69, 287 (1978).
64. A. R. Miedema and R. Boom, Z. Metallkd. 69, 183 (1978).
65. G. Ertl, in The nature of the surface chemical bond, eds. T. Rhodin and G. Ertl, (North-Holland, Amsterdam, 1980).
66. D. Tománek, S. Mukherjee, V. Kumar and K. H. Bennemann, Surf. Sci. 114, 11 (1982).
67. A. R. Miedema, Calphad, 1, 341 (1977).
68. K. Sattler, in Electronic and atomic collisions, eds. J. Eichler, I. Hertel and N. Stolterfoht (Elsevier, Amsterdam, 1984) and references therein.

69. P. Wynblatt and R. C. Ku, in Interfacial Segregation, eds. W. C. Johnson and J. M. Blakely (American Society for Metals, Ohio, 1979).
70. P. Oelhafen, private communications and to be published.
71. P. C. Bouten and A. R. Miedema, J. Less Common Met. **71**, 147 (1980).
72. Selected values of the thermodynamic properties of the elements, eds. R. Hultgren et al. (American Society for Metals, Ohio, 1973).
73. P. Oelhafen, J. Phys. F **11**, L41 (1981).
74. A. R. Miedema et al., in Electrochem. Soc. Proc., **77**, 456.
75. N. H. Tsai, F. F. Abraham and G. M. Pound, J. Catal. **50**, 200 (1977).
76. E. E. Latta and H. P. Bonzel, in Interfacial Segregation, eds. W. C. Johnson and J. M. Blakely, (American Society for Metals, Ohio, 1979).
77. J. Sedlacek et al., in Proc. International Conf. on solid surfaces and 3rd European Conf. on Surf. Sci., Cannes, 1980, p.26.
78. D. Tománek, S. Mukherjee and K. H. Bennemann, Phys. Rev. **28**, 665 (1983).
79. S. Mukherjee and K. H. Bennemann, Surf. Sci. **156**, 580 (1985).
80. S. Mukherjee, D. Tománek and K. H. Bennemann, Chem. Phys. Lett. **119**, 241 (1985).
81. P. M. Marcus, J. E. Demuth and D. W. Jepsen, Surf. Sci. **53**, 501 (1975).
82. J. Stöhr, R. Jaeger and T. Kendelewicz, Phys. Rev. Lett. **49**, 142 (1982).
83. M. Decrescenzi, F. Antonangeli, C. Bellini and R. Rosei, Phys. Rev. Lett. **50**, 1949 (1983).
84. K. H. Rieder, Phys. Rev. B **27**, 6978 (1983).
85. D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. **27**, 1520 (1971).
86. T. T. Anh Nguyen, R. Cinti and M. Avignon, in Proc. 7th International Vacuum Cong. and 3rd Int. Conf. Solid surfaces, eds. R. Dobrozemsky et al. (F. Bergen and Söhne, Vienna, 1977).
87. H. D. Hagstrum and G. E. Becker, Phys. Rev. Lett. **22**, 1054 (1969).
88. H. Scheidt, M. Glöbl and V. Dose, Surf. Sci. **123**, L728 (1982).
89. V. Dose, M. Glöbl and H. Scheidt, J. Vac. Sci. Tech. **A1**, 1115 (1983).
90. A. Liebsch, Phys. Rev. B **17**, 1653 (1978).

91. C. S. Wang and A. J. Freeman, Phys. Rev. B 19, 4930 (1979).
92. D. W. Bullett and M. L. Cohen, J. Phys. C 10, 2101 (1977).
93. M. C. Desjonqueres and F. Cyrot-Lackmann, Surf. Sci. 80, 208 (1979).
94. R. W. Godby, G. A. Benesh, R. Haydock and V. Heine, Phys. Rev. B 32, 655 (1985).
95. S. P. Walch and W. A. Goddard, Surf. Sci. 75, 609 (1978).
96. B. Chakraborty, S. Holloway and J. K. Nørskov, Surf. Sci. 152/153, 660 (1985).
97. J. M. Gallagher and R. Haydock, Surf. Sci. 83, 117 (1979).
98. C. W. Bauschlicher and P. S. Bagus, Phys. Rev. Lett. 52, 200 (1984).
99. C. W. Bauschlicher and P. S. Bagus, Phys. Rev. Lett. 54, 349 (1985).
100. C. M. Varma and A. J. Wilson, Phys. Rev. B 22, 3795 (1980).
101. S. Mukherjee, V. Kumar and K. H. Bennemann, submitted for publication.
102. J. K. Nørskov and N. D. Lang, Phys. Rev. B 21, 2131 (1980).
103. M. Van Hove and S. Y. Tong, J. Vac. Sci. Tech. 12, 230 (1975).
104. S. Andersson, P. A. Karlsson and M. Persson, Phys. Rev. Lett. 51, 2378 (1983).
105. E. W. Plummer, B. Tonner, N. Holzwarth and A. Liebsch, Phys. Rev. B 21, 4306 (1980).
106. S. P. Walch and W. A. Goddard, Solid St. Commun. 23, 907 (1977).
107. J. Friedel, in The physics of metals (1. Electrons), ed. J. M. Ziman (Cambridge, 1969).
108. J. K. Nørskov, Phys. Rev. B 26, 2875 (1982).
109. R. Haydock, V. Heine and M. J. Kelly, J. Phys. C 5, 2845 (1972); 8, 2591 (1975).
110. Articles by R. Haydock, V. Heine and M. J. Kelly, in Solid State Physics, 35, eds. H. Ehrenreich, F. Seitz and D. Turnbull, (Academic, New York, 1980).
111. J. C. Slater, Phys. Rev. 81, 385 (1951).
112. J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).
113. D. G. Dempsey, W. R. Grise and L. Kleinman, Phys. Rev. B 18, 1270 (1978). These authors have given the hopping parameters for ferromagnetic nickel. For simplicity we have used the values corresponding to majority-spin band.

114. N. Beer and D. G. Pettifor, in Proceedings of NATO Advanced Study Inst., Ghent, 1982 (Plenum, New York, 1983).
115. L. F. Matheiss, Phys. Rev. B 5, 290 (1972).
116. V. Heine, Phys. Rev. 153, 673 (1967).
117. F. Herman and S. Skillman, Atomic Structure Calculations, (Prentice-Hall, New Jersey).
118. Y. Boudeville, J. Rousseau-Violet, F. Cyrot-Lackmann and S. N. Khanna, J. Physique 44, 433 (1983).
119. J. M. Gallagher, R. Haydock and V. Heine, J. Phys. C 12, L13 (1979).
120. CRC Handbook on Chemistry and Physics (60th Edition), ed. R. C. Weast, (CRC Press, Boca Raton, Florida, 1981).
121. See, for a review on Bethe-lattice : M. F. Thorpe, in Excitations in Disordered Systems, ed. M. F. Thorpe, (Plenum, New York, 1982).
122. H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry (2nd Edition), (D. Van Nostrand Co., New Jersey, 1956).
123. A. C. Aitken, Determinants and Matrices (6th Edition), (Oliver and Boyd, Edinburg, 1949).
124. C. M. M. Nex, J. Phys. A 11, 653 (1978).
125. V. Heine, in Solid State Physics, 35, eds. H. Ehrenreich, F. Seitz and D. Turnbull, (Academic, New York, 1980).

Sugata MUKHERJEE

CURRICULUM VITAE

Born on 11th November 1954 at Calcutta, India.

Secondary and High school at Deoghar, India, 1962 - 1969.

Undergraduate studies for the "Bachelor of Science" degree at Science College, Patna University, 1969 - 1973. Graduation with honours in Physics, 1973.

Graduate studies for the "Master of Science" degree at Patna University, 1973 - 1976. Master of Science in Physics, 1976.

Continuation of study towards the Post-M.Sc. Associateship diploma at Saha Institute of Nuclear Physics, Calcutta, 1976 - 1977. Post-M.Sc. Associateship diploma with the thesis on the subject of Electronic density-of-states of disordered binary alloys, August 1977. Research assistantship at Saha Institute of Nuclear Physics, Calcutta, 1977 - 1978.

Research assistantship at the Institute for Theoretical Physics, Freie Universität Berlin, 1978 - 1985. Beginning of the doctoral work under the guidance of Prof. Dr. K. H. Bennemann, Oct. 1980. Research publications on the subjects of surface segregation in alloys, properties of small metal-clusters and chemisorption on transition-metals.

